







# DYERS' MATERIALS

*AN INTRODUCTION TO THE EXAMINATION  
VALUATION AND APPLICATION OF  
THE MOST IMPORTANT SUBSTANCES USED IN  
DYEING, PRINTING, BLEACHING  
AND FINISHING*

BY

PAUL HEERMANN, PH.D.

TRANSLATED BY

ARTHUR C. WRIGHT, M.A. (OXON.), B.Sc. (LOND.)

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H. B. STOCKS, F.I.C., F.C.S.

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## PREFACE.

THE present work is the outcome of the author's long connection with the chemical textile industries, and is intended to fill the want which he has found of a special text-book on the examination and valuation of the materials used in those industries, which should contain, within a brief compass, the most valuable methods and data for the use of dyers' and technical chemists.

■ The need for a book of this kind appears to be evident, since the ordinary works on technical analysis are not sufficiently specialized; the subject, however, has a constantly increasing interest for the chemist, whilst, on the other hand, usually text-books on dyeing devote most attention to the finctorial side of the matter.

The book is intended primarily for the chemist, since it presupposes a knowledge of the principles of chemical analysis, frequently only indicates common methods, and bestows chief attention on the specific articles and methods of examination. It shou'd, however, be useful also for educational purposes, and may be of service as an adjunct to general analytical text-books, for students in technical schools and colleges, where dyeing, calico-printing, and similar technical subjects are taught.

The processes of dyeing have been excluded from this book, since they form a separate study, and thus need to be treated in a special volume. In view of the

flourishing literature on the methods of dyeing there does not appear to exist a particular want of such a book.

On the other hand, the author has deemed it advisable to preface the special part of the book by a general part dealing with indicators and solutions, and by a short description of the prime necessities of the textile industries—water and the textile fibres. The chapter, usual in detailed text-books, on preparation for analysis, sampling, etc., has been omitted.

Whilst the author hopes that this book will meet with general approval, he will be thankful for hints in regard to possible additions and alterations. Also in this place he wishes to record his best thanks to certain gentlemen who have assisted him by private communications; in particular, his warmest thanks are due to his revered former teacher, Dr. H. Lange, Director of the Crefeld Higher Dyeing School.

THE AUTHOR.

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## CHAPTER I.

### GENERAL.

**Indicators.** The correct choice of an indicator from among the large number known is of great importance if reliable and accurate results are to be obtained. The indispensable indicators are strictly limited in number, and the choice is to some extent a personal matter, although for a certain purpose one may be found to act better than another.

A random use of indicators in technical analysis is not desirable; in order to obtain uniform results it is necessary ~~to~~ use the customary solutions of indicators and not to depart from them without cogent reasons and previous comparative analyses. Otherwise considerable differences may occur (*e.g.*, for instance phenolphthalein and rosolic acid, or phenolphthalein and methyl orange). Further, if the reaction is to show a sharp end-point, the indicator must be absolutely pure, or at least as pure as it can be obtained. This is especially the case with litmus, turmeric, indigo solution, etc.; *e.g.*, Neubauer and von Schroder, and J. König (*Zeits. für angew. Chem.*, 1891, 108) found that certain commercial preparations of indigo carmine were quite useless for titrations with potassium permanganate, since in the end-reaction they did not change sharply from green to yellow, but to uncertain brownish-red shades. The best test of purity is afforded by a practical application.

For purposes of rapid comparison and review, the properties, solutions and reactions of the best-known indicators are given below.

**Litmus.**—A solution of litmus is prepared by treating the solid material with hot water and filtering. The filtrate is acidified with acetic acid and evaporated to dryness. The



dried residue is treated two or three times with hot alcohol, and, after again drying, the residue is dissolved in water in the proportion 1:10, the solution being preserved with a trace of carbolic acid.

Litmus may be used in the cold in the estimation of all mineral acids, oxalic acid, lactic acid, butyric acid, and tartaric acid even in presence of weak bases, *e.g.*, aniline, toluidine, quinoline, etc. It cannot be used for sulphurous, boric, carbonic, phosphoric, silicic, arsenious, or chromic acid or weak organic acids. Some salts, *e.g.*,  $K_2CrO_4$ ,  $Na_2HPO_4$ ,  $Na_2HAsO_4$ , and  $Na_2CO_3$ , are alkaline to litmus, the salts of the heavy metals generally being acid.

*Phenolphthalein.* This is dissolved in alcohol in the proportion 1:100. Phenolphthalein is sensitive to all acids, even weak organic ones and also carbonic acid, therefore it is applicable to the estimation of all acids. It is also useful for estimating free caustic alkali in carbonates, sulphites, silicates, soaps, etc. Sodium carbonate is alkaline to phenolphthalein but the bicarbonate is neutral. It cannot be used in presence of ammonia or boric acid except by special methods. It should be neutralised with alkali before use.

*Methyl Orange.*—This is dissolved in water in the proportion of 1:1000 and neutralised with dilute acid till the solution becomes orange-red. Methyl orange is sensitive to most mineral acids, but is scarcely affected by a few organic acids, and not at all by most organic acids, carbonic, and boric acid, etc., therefore the alkali can be determined in carbonates and in salts of weak organic acids, borates, phosphates, etc. It cannot be used for oxalic acid as it gives a partial reaction.

*Congo Red.*—This is dissolved in 30 per cent. alcohol in the proportion 1:100. It is suitable for the estimation of free sulphuric acid in alum, etc., and also organic acids.

*Rosolic Acid.*—Dissolved in 60 per cent. alcohol in the proportion of 1:100 forms a useful indicator for mineral acids in artificial light which does not affect its colour. It is not suitable for titrating ammonia or organic acids.

*Corallin.*—This is dissolved in water in the proportion

1 : 100 and used in the same way as rosolic acid, the latter, however, is probably the better of the two.

*Phenacetolin*.—This is dissolved in alcohol in the proportion 1 : 200. It is suitable for use in the estimation of carbonates, but cannot be used for organic acids.

*Cochineal and Carminic Acid*.—A solution of cochineal is made by boiling 1 part of the insect with 80 parts of water, or carminic acid 1 part is dissolved in 100 parts of water. The solution may be used in the estimation of alkaline earth carbonates, but is not suitable for alkalis in presence of alumina or organic acids in the presence of iron and alumina.

*Laemoid*. This is dissolved in 20 per cent. alcohol in the proportion 1 : 200. It is suitable for use in the estimation of alkalis, aluminates, calcium and magnesium bicarbonates, borax, alkaline silicates and aluminates. It is not suitable for organic acids.  $\text{Na}_2\text{CrO}_4$ ,  $\text{Na}_2\text{HPO}_4$ ,  $\text{Na}_2\text{HAsO}_4$ , and  $\text{Na}_2\text{SO}_3$  are alkaline to laemoid, the salts of heavy metals being neutral. This indicator is affected by artificial light.

*Turmeric*. An alcoholic solution of the powdered root is prepared. Turmeric is sensitive to both acids and alkalis. It is most useful, however, in the form of a test paper for boric acid, with which, when dried, it gives a bright red coloration, changed to green by caustic soda and to blue by ammonia.

#### STANDARD SOLUTIONS.

The standard solutions, which are in daily use, may either be normal or decinormal, but for certain purposes other strengths such as double normal or semi (half) normal, etc., may be employed. In the latter case the number of c.c. of solution used must be multiplied by the proper factor, in order to obtain the corresponding number of c.c. of normal solution. The one or the other method is preferred according to individual circumstances.

In the preparation of normal or standardised solutions some initial standard substance is required, by means of which the strength of the solution is checked; for this purpose the following substances are used in acidimetry:—

1. Crystallised oxalic acid (to be used with caution, since it may be partially effloresced or contain excess of water, which conditions are not readily recognised).

2. Anhydrous oxalic acid.

3. Fused sodium carbonate (obtained by igniting sodium bicarbonate).

4. Marble.

5. Potassium bitartrate.

6. Sodium chloride.

All these standard substances must be qualitatively tested for purity; in general, those which can be ignited—sodium chloride, carbonate, etc.—are to be preferred, since they cannot contain any unknown quantity of water. When the chemically pure compound has been dissolved, the solution is titrated by it in the known manner, using a sensitive indicator; the opposite solutions are then standardised. This is the case with oxalic acid, soda and potassium tartrate. With sodium chloride a normal or decinormal solution is made, by means of which solutions of silver nitrate and ammonium sulphocyanide are standardised, from which a hydrochloric acid solution is standardised by Volhard's method (hydrochloric acid + excess of silver nitrate, titrated back by ammonium sulphocyanide, using iron alum as indicator).

From each of the acids alkaline solutions may be standardised, and thence other acids diluted if desired, etc.

The standard solutions in common use, the methods of titration and the indicators used, are given in the following table. In the Appendix will be found a table of the atomic weights of the elements; the molecular weights of important compounds and certain gravimetric and volumetric equivalents are given in the text under their particular headings.

*Fehling's Solution.*—Preparation: (a) 34.639 grammes crystallised copper sulphate dissolved to 500; (b) 173 grammes Rochelle salt and 25 grammes caustic potash dissolved to 500 c.c.

Use: Equal volumes of (a) and (b) are mixed before use and boiled with the solution to be tested for dextrose, the presence of which is indicated by a precipitate of cuprous oxide. Qualitative and quantitative.

| A Normal 1 Solution contains Grammes per Litre. | Generally used as  | Original Substance used as a Standard.                | Titrated against                        | Indicator.                    |
|---|--|---|---|-------------------------------|
| Sulphuric acid . . . . .                        | 49.0   | $\frac{1}{2}$ , $\frac{1}{10}$ , $\frac{1}{100}$ N    | Caustic soda                            | Litmus, phenolphthalein, etc. |
| Hydrochloric acid . . . . .                     | 36.4   | $\frac{1}{10}$ N                                      | Do.                                     | Do.                           |
| Nitric acid . . . . .                           | 63.0   | $\frac{1}{10}$ N                                      | Do.                                     | Do.                           |
| Oxalic acid . . . . .                           | 63.0   | $\frac{1}{10}$ , $\frac{1}{100}$ , $\frac{1}{1000}$ N | Do.                                     | Phenolphthalein               |
| Caustic soda . . . . .                          | 40.0   | $\frac{1}{10}$ , $\frac{1}{100}$ , $\frac{1}{1000}$ N | Sulphuric acid, oxalic acid             | Litmus, etc.                  |
| Sodium carbonate . . . . .                      | 53.0   | $\frac{1}{10}$ , $\frac{1}{100}$ N                    | Sodium carbonate, or as above           | Methyl orange                 |
| Ammonia . . . . .                               | 17.0   | $\frac{1}{10}$ , $\frac{1}{100}$ N                    | Oxalic acid, soda, etc.                 | Litmus, lacmoid, turmeric     |
| Silver nitrate . . . . .                        | 170.0  | $\frac{1}{10}$ N                                      | Sodium chloride                         | Neutral potassium chromate    |
| Sodium chloride . . . . .                       | 58.5   | $\frac{1}{10}$ N                                      | Silver nitrate                          | Do.                           |
| Potassium permanganate . . . . .                | 31.6   | $\frac{1}{10}$ , $\frac{1}{100}$ , $\frac{1}{1000}$ N | Oxalic acid, iron wire                  | Is its own indicator          |
| Sodium tetrathionate . . . . .                  | 248  | $\frac{1}{10}$ N                                      | Iodine solution                         | Starch solution               |
| Iodine . . . . .                                | 127  | $\frac{1}{10}$ , $\frac{1}{100}$ , $\frac{1}{1000}$ N | Thiosulphate                            | Do.                           |
| Arsenious acid (sodium arsenite) . . . . .      | 9.5  | $\frac{1}{10}$ N                                      | Iodine solution                         | Do                            |
| Potassium bichromate . . . . .                  | 9.13   | $\frac{1}{10}$ , $\frac{1}{100}$ N                    | Ferrous salt, ferrous ammonium sulphate | Potassium ferricyanide        |
| Indigo solution . . . . .                       | 10 c.c. should correspond to 0.001 gramme $N_2O_5$ . See estimation of $N_2O_5$ under <i>Water</i> . |   | Potassium nitrate solution              | Is its own indicator          |

<sup>1</sup> In the table, and afterwards, N is used as a contraction of normal: thus 2 N sulphuric acid, N sulphuric acid and  $\frac{1}{10}$  N sulphuric acid represent twice normal, normal and decinormal sulphuric acid respectively.

*Nessler's Reagent*.—Preparation: 13 grammes of mercuric chloride are dissolved in 800 c.c. of hot water, 35 grammes of potassium iodide are gradually added until the precipitate redissolves, mercuric chloride solution is then again added drop by drop until a precipitate just remains; 160 grammes of caustic potash are then dissolved in the liquid, which is made up to 1,000 c.c. and the clear yellow solution poured off from the deposit.

Use: Used in the detection and colorimetric estimation of ammonia in neutral or alkaline solution.

*Starch Solution*.—Preparation: (a) 5 grammes of starch are mixed with a little water and gradually introduced into 1,000 c.c. of boiling water, the liquid is boiled for several minutes, allowed to settle and filtered, (b) or soluble starch is used, made (Zulkowsky) by heating starch with chlorine, hydrochloric acid, etc.

Use: Several c.c. are added to the solution in iodometric estimations. Free iodine colours the starch blue.

To be kept in a cool place. Is useless when mould is perceptible. To preserve the solution a trace of carbolic may be added, or the whole may be pasteurised and covered with paraffin. Soluble starch must always be kept moist.

*Starch and Potassium Iodide Solution*. Preparation: Add a few crystals of potassium iodide to the above starch solution.

Use: A reagent for nitrous acid, free chlorine, etc. Frequently used as potassium iodide starch paper.

To be used with discretion, since ferric chloride also gives the reaction.

*Starch and Zinc Iodide Solution*.—Preparation: 4 grammes of starch are ground and gradually added to a boiling solution of 20 grammes of zinc chloride in 100 c.c. of water; after heating some time, until almost clear, the solution is diluted, 2 grammes of zinc iodide added and the volume made up to 1,000 c.c.

Use: A starch and potassium iodide solution.

Should give no blue coloration with dilute sulphuric acid. Must be kept in the dark.

*Uranium Acetate Solution*.—Preparation: About 35

grammes of uranium acetate are dissolved in water containing acetic acid, the solution made up to 1,000 c.c., allowed to stand several days, filtered and standardised against a solution of phosphoric acid.

Use: Used in the estimation of phosphoric acid.

*Iron Ammonium Alum.* Use. 0.5 c.c. of cold saturated aqueous solution is added in titrating chlorine and copper by Volhard's method.

*Potassium Sulphocyanide Solution.*—Preparation: 1 gramme dissolved into 10 c.c. of water.

Use: An extremely delicate reagent for ferric salts; used in colorimetric estimation of iron.

*Schweitzer's Reagent.*—Preparation Solution, copper hydroxide in ammonia.

Use: A solvent for cellulose, cotton and silk.

*Millon's Reagent.*—Preparation: 10 grammes mercury + 25 grammes nitric acid (1.185) + 25 c.c. water, dissolved lukewarm; this solution mixed with a solution of 10 grammes mercury in 22 grammes nitric acid (1.25 - 1.3 sp. gr.) made on the water-bath.

Use: Reagent for albumins.

*Dobbin's Reagent.*—Preparation Mercuric chloride solution is added to a solution of 5 grammes of potassium iodide until a permanent precipitate just appears; the solution is filtered, 1 gramme of ammonium chloride is added, and then dilute caustic soda until a permanent precipitate again forms, the liquid is filtered and made up to 1,000 c.c.

Use: Reagent for traces of fixed caustic alkalis (in soda, soap, etc.).

*Diphenylamine Solution.* Preparation 2 grammes of diphenylamine are dissolved in 100 c.c. of hot dilute sulphuric acid (1.3), 300 c.c. of strong sulphuric acid (1.84) are then added.

Use: Extremely sensitive reagent for traces of nitrates, nitric acid, peroxides, free chlorine.

A few drops of the solution to be tested are added to about 20 drops of the reagent, the mixture is shaken for one minute. Oxalic acid must be absent.

*M-phenylenediamine Solution.*—Preparation: 5 grammes

are dissolved in water, sulphuric acid is added to acid reaction and the solution made up to 1,000 c.c.

Use: Reagent for nitrous acid.

Useful when iron salts prevent the employment of starch and potassium iodide solution.

*Stannous Chloride Solution.*—Preparation: 1 part of crystallised stannous chloride dissolved in 2 parts of hydrochloric acid (1·19).

Use: Bettendorf's reagent for arsenic.

*Alkaline Lead Solution.*—Preparation: 1 part of lead acetate is dissolved in 10 parts of distilled water and caustic soda added until the precipitate just redissolves.

Use: Reagent for sulphuretted hydrogen.

*Potassium Bichromate Solution.*—Preparation: A solution containing 3·874 grammes of pure fused potassium bichromate in 1,000 c.c.

Use: To control the strength of standard sodium thiosulphate solution. 20 c.c. of this solution liberate 0·2 gramme of iodine (in sulphuric acid solution, containing 1 to 2 grammes of potassium iodide), which is titrated with sodium thiosulphate solution.

*Sodium Nitroprusside Solution.* Preparation: 1 part of sodium nitroprusside dissolved in 50 parts of water.

Use: Delicate reagent for sulphuretted hydrogen and alkaline sulphides.

*Indigo Solution.*—Preparation: Indigotin dissolved in fuming sulphuric acid, and the solution diluted so that 10 c.c. = 0·001 gramme  $N_2O_5$ .

Use: Estimation of nitric acid and nitrates, estimation of oxygen in water.

Chlorates and free chlorine disturb the reaction.

*Potassium Nitrate Solution.*—Preparation: A solution containing 0·1872 gramme of pure potassium nitrate in 1,000 c.c.

Use: In standardising the above indigo solution, 10 c.c. of potassium nitrate solution contain 0·001 gramme  $N_2O_5$ .

See estimation of nitric acid, under Water.

*Barium Chloride Solution.*—Preparation: A solution containing 0·523 gramme of crystallised  $BaCl_2 \cdot 2H_2O$  in 1,000 c.c.

Use: See determination of hardness of water.

100 c.c. = 12° (German) of hardness.

*Ammonium Molybdate Solution.*—Preparation: 1 part of molybdic acid dissolved in 4 parts of ammonia (8 per cent.  $\text{NH}_3$ ) and the solution poured into 15 parts of nitric acid (sp. gr. 1.2); or 150 grammes of pure ammonium molybdate dissolved by heating in 1,000 c.c. of water, and mixed with 1,000 c.c. of nitric acid (1.2). Allow to stand for several days in a moderately warm place, and, if necessary, pour off from the deposit.

Use: Used in the detection and estimation of phosphoric acid. To be kept in the dark (Presenius, *Quant. Anal.*, 11, 540).



## CHAPTER II.

### PRIMARY MATERIALS.

#### WATER.

It is sufficiently well known that water plays an all-important part in dyeing. Now the iron, then the lime, or again the sulphuric acid has a disturbing action. The essential characteristics of water required for household and technical purposes are quite different. For the former purpose even traces of ammonia and nitrous acid make a water appear at least suspicious, and, on the other hand, a certain quantity of iron and a considerable degree of hardness are quite harmless and even to some extent impart a pleasant flavour. For technical purposes traces of ammonia, etc., are quite unimportant; the principal attention must be given to the hardness and iron content. The hardness of water is known to produce boiler scale, which causes loss of heat, renders boiler explosions possible, and in any case shortens the life of the boiler. Iron on its part injures the dyes and causes spots; it is especially harmful in Turkey-red dyeing and in bleaching. Definite limits for the permissible amount of impurities in water for technical or household use cannot be laid down; the whole of the circumstances must be taken into consideration in deciding whether a water may be used, how and to what extent it is to be purified, etc. Purification is naturally avoided as far as possible, since it is a costly process: a good system applied to an average water of 10° of hardness (German) costs about 1 farthing per cubic metre.

*Appearance.*—Clear or turbid, colourless or, coloured.

Compare in a glass tube 70 cm. long, 20 mm. wide, with distilled water.

*Smell*.—Examine at 40° to 50°C. (coal gas, sulphuretted hydrogen).

*Taste*.—Examine at 15° to 20° C.

*Reaction*.—Litmus and turmeric paper, cold and hot.

*Ammonia*.—Qualitatively, by means of Nessler's reagent (which see). Quantitatively, by the colorimetric process, in comparison with an ammonium chloride solution containing 3.147 grammes per litre, 1 c.c. of which contains 1 milligramme of ammonia ( $\text{NH}_3$ ) (J. König, *Chem. Zeit.*, 1897, 599; *J. S. C. I.*, 1897, 936).

*Nitrous Acid*.—Qualitatively, by means of potassium iodide and starch solution; in the presence of iron salts, by means of *m*-phenylenediamine solution. Quantitatively by a colorimetric process against a solution containing a definite quantity of  $\text{N}_2\text{O}_3$  (0.406 gramme silver nitrite with excess of sodium chloride in 1,000 c.c., the filtered solution contains 0.1 milligramme  $\text{N}_2\text{O}_3$  in 1 c.c.) (J. König, *loc. cit.*).

*Carbonic Acid*.—Detected by lime water.

*Sulphuretted Hydrogen*. Detected by means of lead acetate paper.

*Lead and other heavy metals*. Detected by means of sulphuretted hydrogen water.

*Nitric Acid*.—Qualitatively, by means of diphenylamine solution. Quantitatively, see below.

**Hardness of Water.**—This property is variously expressed in different countries.

English scale, 1° = 1 grain  $\text{CaCO}_3$  in 1 gallon of water.

German „ 1° = 1 part  $\text{CaO}$  in 100,000 parts of water.

French „ 1° = 1 part  $\text{CaCO}_3$  in 100,000 parts of water.

| English. | German. | French. |
|----------|---------|---------|
| 0.70     | 0.56°   | 1       |
| 1.25     | 1°      | 1.71°   |
| 1°       | 0.8°    | 1.43°   |

A distinction is made between “total” and “permanent” hardness; when the expression “hardness” is not qualified, total hardness is always understood. Total hardness is the

hardness of the untreated water; permanent hardness is that of the water after boiling ten to fifteen minutes, replacing the evaporated water, and filtering. The difference is known as temporary hardness. Both total and permanent hardness are determined with the same solutions.

1. Gravimetric estimations of lime and magnesia, calculation of the magnesia into the equivalent quantity of lime (see p. 16); the sum, expressed as parts of CaO in 100,000 parts of water, gives the hardness on the German scale.

2. Acidimetric estimation: 100 to 200 c.c. of water are evaporated with excess of sodium carbonate to 25 c.c., the resulting alkaline earth carbonates are filtered off, washed to neutral reaction, and titrated together with the filter paper in a porcelain dish with  $\frac{1}{10}$  N nitric acid; 1 c.c.  $\frac{1}{10}$  N acid = 0.005 gramme  $\text{CaCO}_3$  = 0.0028 gramme CaO. Or the carbonates are dissolved in excess of N, HCl and titrated back with NaHO.

3. Titration with a standard soap solution (the methods of Faisst, Knauss and Clark).

(a) 0.523 gramme of pure crystallised barium chloride is dissolved and the solution made up to 1,000 c.c.; the quantity of barium chloride contained in 100 c.c. of this solution corresponds to 12° of hardness (German).

0.2 gramme pure  $\text{CaCO}_3$  dissolved in HCl, evaporated off acid and made up to 1,000 c.c. 50 c.c. of this solution is made equivalent to 14.25 c.c. soap solution (Clark). A table is used for estimating degrees of hardness, see below.

(b) 20 grammes of pure soap are dissolved in 1,000 c.c. of alcohol (56 per cent. by volume).

Solution (b) is now standardised against (a): 100 c.c. of the latter are brought into a stoppered bottle of about 200 c.c. capacity, the soap solution is gradually added from a burette until, after violent shaking, the foam remains for five minutes. The soap solution is then diluted with 56 per cent. alcohol, in accordance with the volume used in the experiment, so that 45 c.c. exactly correspond to 100 c.c. of the barium chloride solution. Now 100 c.c. of the water under examination are titrated with this soap solution in the same manner as the 100 c.c. of barium chloride solution, i.e., the soap

solution is gradually run from a burette into 100 c.c. of the water, with violent shaking, until the froth endures for five minutes. The hardness of the water, which is not proportional to the soap used, is obtained from the table below. In case more than 45 c.c. of the soap solution are required, the water under examination must be proportionately diluted with distilled water.

*Table of Hardness (German).*

| Soap Solution<br>c.c. | Hardness<br>degrees<br>(German) | Soap Solution<br>c.c. | Hardness<br>degrees<br>(German) | Soap Solution<br>c.c. | Hardness<br>degrees<br>(German) |
|-----------------------|---------------------------------|-----------------------|---------------------------------|-----------------------|---------------------------------|
| 3.4                   | 0.5                             | 18.9                  | 1.5                             | 34.7                  | 8.9                             |
| 4.2                   | 0.7                             | 19.7                  | 1.7                             | 35.3                  | 9.1                             |
| 5.0                   | 0.9                             | 20.4                  | 1.9                             | 36.0                  | 9.3                             |
| 5.8                   | 1.1                             | 21.2                  | 5.1                             | 36.7                  | 9.5                             |
| 6.6                   | 1.3                             | 21.9                  | 5.3                             | 37.4                  | 9.7                             |
| 7.4                   | 1.5                             | 22.6                  | 5.5                             | 38.1                  | 9.9                             |
| 8.2                   | 1.7                             | 23.3                  | 5.7                             | 38.8                  | 10.0                            |
| 9.0                   | 1.9                             | 24.0                  | 5.9                             | 38.7                  | 10.1                            |
| 9.8                   | 2.1                             | 24.8                  | 6.1                             | 39.4                  | 10.3                            |
| 10.5                  | 2.3                             | 25.5                  | 6.3                             | 40.1                  | 10.5                            |
| 11.3                  | 2.5                             | 26.2                  | 6.5                             | 40.8                  | 10.7                            |
| 12.1                  | 2.7                             | 26.9                  | 6.7                             | 41.5                  | 10.9                            |
| 12.8                  | 2.9                             | 27.6                  | 6.9                             | 42.1                  | 11.1                            |
| 13.6                  | 3.1                             | 28.4                  | 7.1                             | 42.4                  | 11.2                            |
| 14.3                  | 3.3                             | 29.1                  | 7.3                             | 42.8                  | 11.3                            |
| 15.1                  | 3.5                             | 29.8                  | 7.5                             | 43.1                  | 11.4                            |
| 15.9                  | 3.7                             | 30.5                  | 7.7                             | 43.4                  | 11.5                            |
| 16.6                  | 3.9                             | 31.2                  | 7.9                             | 43.7                  | 11.6                            |
| 17.4                  | 4.1                             | 31.9                  | 8.1                             | 44.0                  | 11.7                            |
| 17.8                  | 4.2                             | 32.6                  | 8.3                             | 44.4                  | 11.8                            |
| 18.1                  | 4.3                             | 33.3                  | 8.5                             | 44.7                  | 11.9                            |
| 18.5                  | 4.4                             | 34.0                  | 8.7                             | 45.0                  | 12.0                            |

**Total Solids.**—100 to 250 c.c. of the water are evaporated in a platinum or porcelain dish on the water-bath, the residue dried at 105° C., weighed, and calculated to 100,000 parts. The residue may be ignited (see *Organic Matter*) and be used in the estimation of iron.

**Chlorine.**—25, 50 or 100 c.c. of the water are titrated by  $\frac{1}{10}$  N silver nitrate solution, with neutral potassium chromi-

*English Table of Hardness (Clark's). (50 c.c. of Water taken.)*

| c.c. of Soap Solution. | CaCO <sub>3</sub> per 100,000 | c.c. of Soap Solution | CaCO <sub>3</sub> per 100,000 | c.c. of Soap Solution | CaCO <sub>3</sub> per 100,000 | c.c. of Soap Solution | CaCO <sub>3</sub> per 100,000 | c.c. of Soap Solution | CaCO <sub>3</sub> per 100,000 |
|------------------------|-------------------------------|-----------------------|-------------------------------|-----------------------|-------------------------------|-----------------------|-------------------------------|-----------------------|-------------------------------|
| .7                     | .00                           | 3.8                   | 4.29                          | 6.9                   | 8.71                          | 10.0                  | 13.31                         | 13.1                  | 18.17                         |
| .8                     | .16                           | .0                    | .48                           | 7.0                   | .86                           | .1                    | .46                           | .2                    | .88                           |
| .9                     | .32                           | 4.0                   | .57                           | .1                    | 9.00                          | .2                    | .61                           | .3                    | .49                           |
| 1.0                    | .48                           | .1                    | .71                           | .2                    | .14                           | .3                    | .76                           | .4                    | .65                           |
| .1                     | .63                           | .2                    | .86                           | .3                    | .29                           | .4                    | .91                           | .5                    | .81                           |
| .2                     | .79                           | .3                    | 5.00                          | .4                    | .43                           | .5                    | 14.06                         | .6                    | .97                           |
| .3                     | .95                           | .4                    | .14                           | .5                    | .57                           | .6                    | .21                           | .7                    | 19.18                         |
| .4                     | 1.11                          | .5                    | .29                           | .6                    | .71                           | .7                    | .37                           | .8                    | .29                           |
| .5                     | .27                           | .6                    | .43                           | .7                    | .86                           | .8                    | .52                           | .9                    | .44                           |
| .6                     | .43                           | .7                    | .57                           | .8                    | 10.00                         | .9                    | .68                           | 14.0                  | .60                           |
| .7                     | .56                           | .8                    | .71                           | .9                    | .15                           | 11.0                  | .84                           | .1                    | .76                           |
| .8                     | .69                           | .9                    | .86                           | 8.0                   | .30                           | .1                    | 15.00                         | .2                    | .94                           |
| .9                     | .82                           | 5.0                   | 6.00                          | .1                    | .45                           | .2                    | .16                           | .3                    | 20.08                         |
| 2.0                    | .95                           | 1                     | .14                           | .2                    | .60                           | .3                    | .32                           | .4                    | .24                           |
| .1                     | 2.08                          | .2                    | .29                           | .3                    | .75                           | .4                    | .48                           | .5                    | .40                           |
| .2                     | .21                           | .3                    | .43                           | .4                    | .90                           | .5                    | .63                           | .6                    | .56                           |
| .3                     | .34                           | .4                    | .57                           | .5                    | 11.05                         | .6                    | .79                           | .7                    | .71                           |
| .4                     | .47                           | .5                    | .71                           | .6                    | .20                           | .7                    | .95                           | .8                    | .87                           |
| .5                     | .60                           | .6                    | .86                           | .7                    | .35                           | .8                    | 16.11                         | .9                    | 21.03                         |
| .6                     | .74                           | .7                    | 7.00                          | .8                    | .50                           | .9                    | .27                           | 15.0                  | .19                           |
| .7                     | .86                           | .8                    | .14                           | .9                    | .65                           | 12.0                  | .43                           | .1                    | .35                           |
| .8                     | .99                           | .9                    | .29                           | 9.0                   | .80                           | .1                    | .59                           | .2                    | .61                           |
| .9                     | 3.12                          | 6.0                   | .43                           | .1                    | .95                           | .2                    | .75                           | .3                    | .68                           |
| 3.0                    | .38                           | .1                    | .57                           | .2                    | 12.11                         | .3                    | .90                           | .4                    | .85                           |
| .1                     | .51                           | .2                    | .71                           | .3                    | .26                           | .4                    | 17.06                         | .5                    | 22.02                         |
| .2                     | .64                           | .3                    | .86                           | .4                    | .41                           | .5                    | .22                           | .6                    | .18                           |
| .3                     | .77                           | .4                    | 5.00                          | .5                    | .56                           | .6                    | .38                           | .7                    | .35                           |
| .4                     | .90                           | .5                    | .14                           | .6                    | .71                           | .7                    | .54                           | .8                    | .52                           |
| .5                     | 4.03                          | .6                    | .29                           | .7                    | .86                           | .8                    | .70                           | .9                    | .69                           |
| .6                     | .16                           | .7                    | .43                           | .8                    | 13.01                         | .9                    | .86                           | 16.0                  | .86                           |
| .7                     |                               | .8                    | .57                           | .9                    | .16                           | 13.0                  | 18.02                         |                       |                               |

ate as indicator, until a brown coloration just occurs. The result is calculated to 100 litres. 1 c.c.  $\frac{1}{10}$  N silver solution = 0.00354 gramme of chlorine.

**Nitric Acid** (Trommsdorff-Marx). — 10 or 25 c.c. of the water are titrated in a small flask with indigo solution until, on the addition of 20 c.c. of mixed fuming and ordinary sulphuric acid, the initial temperature of the mixture being 180° C., the liquid just appears slightly green. This estimation must be performed several times, first approximately, then accurately. It is important that the indigo solution be added *first*, and *then* the sulphuric acid (in the first rough experiment the sulphuric acid may be added first and the mixture titrated with indigo solution). When the solution, after shaking with sulphuric acid, still appears yellow, the experiment must be repeated with more indigo solution, until the point is hit at which a green coloration appears on shaking with sulphuric acid (see *Indigo Solution*).

The acid should be tested to see that it is free from nitrates.

Nitric acid in other salts may also be estimated by this process.

The results are accurate only at great dilutions, the water must be proportionately diluted when more than 3 milligrammes of  $N_2O_5$  are contained in 25 c.c.

Example: for 10 c.c. of water, 10 c.c. of indigo solution are used (7 c.c. of indigo solution = 1 milligramme  $N_2O_5$ );  $7:1=10:x$ , or  $x=1.43$ . Thus in 10 c.c. of water there is 1.43 milligramme  $N_2O_5$ , or in 100 litres of water 14.3 grammes  $N_2O_5$ .

**Gravimetric Estimations** ( $SiO_2$ ,  $Fe_2O_3$ ,  $Al_2O_3$ ,  $CaO$ ,  $MgO$ ,  $SO_3$ ).

**Silica.** 2 litres of water (I. and II.) are evaporated separately, the residues moistened with a little strong hydrochloric acid, evaporated and heated for two hours at 105° C. in order to render the silica insoluble. The residues, I. and II., are taken up in hot dilute hydrochloric acid, the silica brought on to an ash-free filter paper, which is dried, ignited, and the residue calculated as  $SiO_2$  per 100 litres.

*Iron and Alumina.*—The filtrate from the  $\text{SiO}_2$  of litre I. is precipitated with ammonia, heated for some time to drive off the greater part of the ammonia, the precipitate allowed to settle, the liquid decanted off, filtered, the residue washed with hot water, ignited and weighed =  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ .

*Iron.*—In the precipitate, or in a residue obtained by evaporating the water, the iron is determined colorimetrically; the alumina is then calculated by difference (iron and aluminium may also be separated, *e.g.*, by treating the hydrochloric acid solution with excess of caustic soda, in which alumina is soluble, but ferric hydroxide insoluble).

*Lime.* The filtrate from iron and aluminium is made ammoniacal, ammonium oxalate added, the liquid left for some hours on the water-bath, filtered after twelve hours, the precipitate dried and ignited, finally before the blowpipe to constant weight. It is weighed as  $\text{CaO}$  and calculated to 100 litres (to check the result it may be converted into  $\text{CaSO}_4$ ) or  $\text{CaCO}_3$  as the case may be.

*Magnesia.* The filtrate from the lime is allowed to stand for twelve hours in the cold with ammonium chloride, ammonia and sodium phosphate. The precipitate is filtered off, ignited and weighed. The pyrophosphate,  $\text{Mg}_2\text{P}_2\text{O}_7$ , obtained is now calculated to  $\text{MgO}$  and reduced to 100 litres.

*Sulphuric Acid.*—The filtrate from the silica of litre II. is precipitated boiling with excess of barium chloride after addition of hydrochloric acid. The precipitate is filtered off, ignited, weighed, and the barium sulphate obtained calculated to  $\text{SO}_3$  per 100 litres.

*Carbonic Acid.*—The carbonic acid contained in water is not of much importance in dyeing. The carbonates can be determined by direct titration of 500 c.c. of the water with  $\frac{1}{10}$  N hydrochloric acid and methyl orange. Allowance must be made for the sensibility correction of the indicator. 1 c.c. of  $\frac{1}{10}$  N acid = 0.0022 gramme  $\text{CO}_2$ .

Free carbonic acid, present along with the carbonates, is best determined by Pettenkofer's method: 100 c.c. of water are mixed in a flask with 3 c.c. of strong barium

chloride solution, 2 c.c. of ammonium chloride solution, and 45 c.c. of standardised baryta solution, the flask is well corked, shaken, and allowed to stand until the precipitate has settled. An aliquot portion (50 or 75 c.c.) of the clear solution is titrated with  $\frac{1}{10}$  N nitric acid, the result calculated to the whole volume, i.e. 150 c.c., and deducted from the 45 c.c. of baryta solution or the equivalent amount of nitric acid.

Example: 45 c.c. of baryta water are equivalent to 40 c.c. of  $\frac{1}{10}$  N nitric acid; 50 c.c. of the clear solution require 10 c.c. of  $\frac{1}{10}$  N acid;  $40 - 10 \times 3 = 90$  c.c. of  $\frac{1}{10}$  N acid per 100 c.c. of water = 1.98 gramme of  $\text{CaO}$  in 1 litre of water.

**Organic Matter.**—(a) Approximately by igniting the residue obtained on evaporation, moistening with ammonium carbonate and again igniting gently. The loss in weight is organic matter.

(b) More accurately by titration with potassium permanganate: 100 c.c. of the water (measured in a graduated flask, not by a pipette) are boiled in a 300 c.c. flask with 10 c.c. of dilute sulphuric acid (1:4) and 10 or 20 c.c. of  $\frac{1}{100}$  N potassium permanganate solution, for exactly ten minutes, reckoning from the commencement of ebullition. The colour must be distinctly red at the conclusion, otherwise more permanganate must be used. The solution is then cooled to 60° to 70° C., decolourised with  $\frac{1}{100}$  N oxalic acid (10 or 20 c.c.) and titrated back with  $\frac{1}{100}$  N permanganate until the pink coloration is permanent.

The result is generally expressed in grammes of permanganate required by 100 litres of water. 1 c.c. of  $\frac{1}{100}$  N permanganate = 0.000316 gramme of  $\text{MnO}_4$  per 100 c.c., or 0.316 gramme per 100 litres of water. The calculation as organic matter is very properly being abandoned, since its value is problematical, in view of the very varying amounts of permanganate required by different organic compounds.

If the water contains much nitrite, 1.66 part of permanganate must be deducted for 1 part of  $\text{N}_2\text{O}_3$ . If it contains considerable quantities of ammonia, this must be removed by a preliminary evaporation to about half the volume, the evaporated water being then replaced by distilled.



Volatile organic matter would, however, thus be lost.

As a rule, in dyeing, the quantity of organic matter is without importance. Isolated cases have been observed in which an abnormal quantity of organic matter decomposed certain artificial dyes or brought about reduction in mordanting wool with potassium bichromate (*Leipz. Färbzeit.*, 1897, 8, 88).

*Average Values.*—To how great an extent the composition of water varies with its source will be seen from the figures given in the following table, which were obtained by an English commission as the average values of 600 usable waters. The figures represent grammes per 100,000 parts of water.

*Average Values Obtained by the English Pollution of Rivers Commission.*

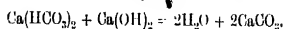
|                      | Total Solids. | Organic Carbon. | Organic Nitrogen. | Ammonia | Nitrogen as Nitrates and Nitrites. | Total Nitrogen. | Chlorine | Hardness. |        |
|----------------------|---------------|-----------------|-------------------|---------|------------------------------------|-----------------|----------|-----------|--------|
|                      |               |                 |                   |         |                                    |                 |          | Perman.   | Total. |
| Rain water           | 2.95          | 0.07            | 0.015             | 0.029   | 0.003                              | 0.042           | 0.822    | 0.5       | 0.8    |
| Upland Surface water | 9.67          | 0.322           | 0.032             | 0.002   | 0.009                              | 0.042           | 1.13     | 4.3       | 5.4    |
| Deep Well water      | 43.78         | 0.061           | 0.018             | 0.012   | 0.495                              | 0.522           | 5.11     | 9.2       | 25.0   |
| Spring water         | 28.20         | 0.056           | 0.013             | 0.001   | 0.383                              | 0.396           | 2.49     | 7.5       | 18.5   |

**Water Purification.**—Water may be purified by various methods, mechanical and chemical.

The mechanical purification of water is accomplished by allowing it to flow through a number of filtering layers, by which the suspended particles are retained. For example, a Berlin municipal filter is composed as follows: 0.3 m. of clay, 0.15 m. of linen, 0.3 m. of gravel and coarse sand, 0.45 m. of fine sand; the Altona filter contains 2.2 m. of pebbles the size of a fist, 7.5 m. of coarse gravel, 7.5 m. of fine gravel and 0.9 m. of fine sand.

By chemical purification dissolved constituents are wholly or partially eliminated.

1. Lime or lime water, added in proportion to the temporary hardness; excess of lime is to be avoided.



2. Water glass, especially used for waters with great permanent hardness; for each 1° of hardness and 100 litres of water, 3 grammes of water glass and 3 grammes of calcined soda are used. Since the precipitate settles very slowly the water must be filtered.

3. Soda and soap, in silk-dyeing. The water is boiled and the scum removed.

4. Barium salts.  $\text{BaCO}_3 + \text{CaSO}_4 = \text{BaSO}_4 + \text{CaCO}_3$ . The disadvantage is that barium carbonate is dissolved by free carbonic acid and the water is thus made poisonous if barium is in excess.

5. Ammonium oxalate is poisonous, and, since excess is unavoidable, should not be used.

6. Alum: not suitable, since potassium and ammonium salts are introduced.

7. Aluminium sulphate: good action on waters which are coloured. Excess increases the permanent hardness.

8. Ferric chloride, ferrous sulphate.

9. Metallic iron. 1 kilo. of iron wire is used to 100,000 litres of water, ferric hydroxide being formed. Not suitable, since filtering is necessary.

In addition to these systematic methods of purifying water, various so-called "boiler fluids" have been proposed and brought on to the market. Generally speaking (1) they make soluble those salts contained in the water which form boiler scale, or (2) cause the scale to be friable and therefore readily removed, thus increasing the life and safety of the boiler. The substances used for this purpose act mechanically or chemically, the former by contact prevent the precipitation or cause the scale to deposit in a less dangerous condition, whilst the latter enter into chemical reactions with the salts in the water. The following list contains the most important anti-incrustators, mixtures of which in the most varied proportions are used:—

Soda, ammonium chloride, barium chloride, stannous chloride, caustic soda, lime, hydrochloric acid, tannic acid,

catechu, oak and pine sawdust, slimy substances, potato chips, dextrine, flour, bran, resin, pitch, clay, paraffin, petroleum and numerous other substances.

The water may also be corrected in the dye-bath itself; this is best done with acetic acid, which is added in quantity equivalent to the temporary hardness. For every 2° of temporary hardness 85 to 86 c.c. of commercial acetic acid are added per cubic metre. If too much acetic acid is added, the formation of the lakes of the colouring matters takes place very slowly, and long boiling is necessary (see also Francis Wyatt, *Eng. and Mining Journal*, 1895, 60, 220; Nosselt, *Zeits. d. V. d. Ingenieure*, 1895, 39, 991; E. Schleh, *Das Wasser und der Kesselstein*, published by E. Mayer, Aix-la-Chapelle, 1897).

#### Technical Examination of the Suitability of a Water.—

Whether a water is suitable for use in dyeing and printing for one purpose or another, and to what extent it influences the shades, can be suitably ascertained by making comparative dyeing, etc., trials with distilled water and the water under examination.

For such an experiment 30 to 40 litres of water are generally sufficient, in which cotton, wool or silk is mordanted, dyed, printed, washed, etc. If the shades turn out worse than those obtained with distilled water, then the water must be condemned, otherwise it is to be regarded as suitable. For such experiments, logwood, fustic, vesuvine and safranine, among others, are suitable (see H. Lange, *Farberzeit.*, 1891, No. 23, and A. Lehmann, *ibid.*, 1895, No. 34, p. 378).

**Effluents.**—In the examination of effluents, the corrosive, malodorous and poisonous constituents receive the first attention. Thus, in the first place, the acidity or alkalinity, then the presence or absence of sulphuretted hydrogen, substances producing that gas, and in general substances of bad odour, and finally the presence or absence of poisonous matters (lead, arsenic, aniline, etc.), must be ascertained.

As with water for use, the following constituents also serve to characterise an effluent: residue on evaporation, organic matter, suspended matter, lime, magnesia, chlorine, sulphuric acid, ammonia, nitric acid, nitrous acid, phosphoric acid, etc.

(cf. F. Fischer, *Zeits. angew. Chem.*, 1890, 64; J. S. C. I., 1890, 93, and J. König, *Zeits. angew. Chem.*, 1890, 88).

### TEXTILE FIBRES: CHEMICAL EXAMINATION.

#### 1. Detection of Cellulose, Wood Fibre, Lignified Fibre.—

Iodine solution and sulphuric acid mixture.

(a) One gramme of potassium iodide dissolved to 100 c.c. of water, iodine then added to saturation (excess remains at the bottom of the solution).

(b) Three volumes of strong sulphuric acid are slowly added, with cooling, to a mixture of 2 volumes of the purest glycerin and 1 volume of distilled water.

The test is carried out as follows. The fibre under examination is moistened on the slide with a few drops of the above iodine solution, the excess removed after some time by means of filter-paper and one to two drops of solution (b) added. Pure cellulose does not swell and is coloured pure blue; lignified fibres are coloured yellow.

#### 2. Detection of Cellulose. Zinc chloride iodine solution.

In place of the above two solutions a solution of iodine and zinc chloride may be used, which colours cellulose reddish to bluish-violet. A solution of iodine in potassium iodide solution is mixed with strong zinc chloride solution (according to von Hohnel, 1 part of iodine, 5 parts of potassium iodide, 30 parts of zinc chloride and 14 parts of water; or 100 parts of  $ZnCl_2$  of sp. gr. 1.82 + 12 parts of  $H_2O$  + 6 parts of KI + iodine, until iodine vapours are evolved).

3. Detection of Lignified Fibres.—An aqueous solution of indol, followed by the addition of hydrochloric acid (red coloration); aniline sulphate or hydrochloride, followed by dilute hydrochloric acid (golden-yellow coloration); phloroglucinol and hydrochloric acid (red coloration), naphthylamine hydrochloride (orange coloration).

Sections of jute give no colour reactions with these reagents, whilst they are coloured a fine yellow by No. 1 (iodine solution and sulphuric acid).

4. Detection of Cotton and Lignified Fibres.—Ammoniacal copper oxide. Freshly precipitated copper hy-

dioxide is dissolved in strong ammonia, and the solution kept in dark, well-stoppered bottles. The solution at once dissolves dry cotton; cellulose, slightly lignified fibres (hemp), swell considerably or dissolve; strongly lignified fibres barely swell.

**5. Detection of Animal or Vegetable Fibre.**—Naphthol solution, 0.01 gramme of pure fibre is treated with 1 c.c. of water and 2 drops of a 15 to 20 per cent. alcoholic solution of  $\alpha$ -naphthol, 1 c.c. of strong sulphuric acid is then added. If a vegetable fibre is present, a deep violet solution is formed on shaking; animal fibres give a yellowish-reddish brown coloration (the fibre remains undissolved). If thymol be used instead of  $\alpha$ -naphthol, the solution becomes red.

The following conclusions may be drawn, based upon the coloration and the solubility or insolubility of the fibre.

| Violet Coloration.            |   | Slight or no Coloration.      |                       |
|-------------------------------|---|-------------------------------|-----------------------|
| The fibre dissolves at once   | vegetable fibre alone or mixed with silk.             | The fibre dissolves at once   | silk.                 |
|                               | vegetable fibre mixed with wool or perhaps with silk. | The fibre does not dissolve   | wool.                 |
| The fibre partially dissolves | vegetable fibre mixed with wool or perhaps with silk. | The fibre partially dissolves | wool mixed with silk. |

**6. Detection of Animal and Vegetable Fibres.**—A caustic soda or potash solution of 8 per cent. strength ( $6^{\circ}$  to  $7^{\circ}$  B. = 1.04 sp. gr.) dissolves animal fibres, whilst vegetable fibres remain almost unattacked. Wool dissolves in five minutes, silk in ten to fifteen minutes at water-bath temperatures.

The following method for estimating cotton in woollen fabrics is official in Germany: to 5 grammes of woollen yarn contained in a beaker of 1 litre capacity are added 200 c.c. of 10 per cent. caustic soda solution; the liquid is slowly (in about twenty minutes) brought to the boil over a small flame and then maintained gently boiling for fifteen minutes longer. The wool is then completely dissolved (dressed woollen yarn must previously be treated with 3 per cent. hydrochloric acid and washed with hot water). When the wool is dissolved, the liquid is filtered through a weighed Gooch crucible,

which is dried at a gentle heat, allowed to stand a short time in the air, and weighed. The increase in weight of the crucible gives the weight of the cotton fibre.

**7. Detection of Wool and Cotton.**—Rosaniline solution. If wool and cotton be dipped for some seconds in a warm or hot colourless solution of rosaniline containing ammonia, and then washed in the cold, the wool becomes red as soon as all the alkali is removed, whilst the cotton remains colourless. Silk behaves like wool, linen, jute, etc., as cotton. The colourless rosaniline solution is obtained by adding caustic soda or ammonia to a boiling solution of magenta and filtering.

**8. Nitric acid.** Boiling dilute nitric acid colours wool yellow (silk to a less extent), whilst vegetable fibres (cotton, flax, hemp, etc.) remain colourless.

**9. Detection of Silk, Wool, Cotton.** Nitric and sulphuric acids. Silk (and goats' wool) when left for fifteen minutes in a nitrating mixture (equal volumes of strong nitric and sulphuric acids) is completely dissolved; wool is coloured yellow to yellowish-brown; vegetable fibres, on the contrary, are altered neither in colour nor structure (gun-cotton).

**10. Phenomena of Combustion.** Animal fibres burn slowly, since they contain nitrogen, and give off a smell peculiar to many nitrogenous substances (horn, hair, hoofs, etc.). They leave a residue of carbon, which burns with difficulty, and relatively much ash. The volatile products of combustion redden moist turmeric paper. Vegetable fibres burn readily, producing an empyreumatic odour (somewhat like paper), they give little ash and the vapours redden moist neutral litmus paper.

**11. Behaviour towards Various Reagents.**—(a) Silk remains undissolved by sulphuric acid for only a few moments, whilst wool remains longer undissolved. Hence a process for the quantitative separation of silk and wool: dilute the solution and filter.

(b) Silk and vegetable fibres are not coloured by a solution of litharge in caustic soda, whilst wool, on account of the sulphur it contains, is coloured brown.

(c) Ammoniacal copper oxide solution dissolves silk, wool remains undissolved.

(d) A solution of wool in caustic potash gives a violet coloration with sodium nitroprusside.

(e) Wool dissolves in 10 per cent. caustic soda on the water-bath within five minutes, whilst silk requires ten to fifteen minutes for complete solution.

**12. Detection of Cotton and Linen.**—(a) Kindt's test. The fibre, freed from dressing, is placed in strong sulphuric acid for half a minute to two minutes, according to its thickness, it is washed with water, gently rubbed with the fingers, placed in dilute ammonia and dried. Any cotton present is converted by the acid into a jelly, which is removed by the rubbing and washing; linen, on the contrary, is little altered.

(b) The fibre under examination is dipped in olive oil and the excess of oil removed by gentle pressure between filter paper. Linen acquires a gelatinous, translucent appearance (somewhat similar to that of oiled paper), whilst cotton remains unaltered. Hence on a dark background the linen fibres appear dark, the cotton fibres light (Frankenheim and Leykauf).

(c) Rosolic acid test. Linen becomes rose-coloured when treated with an alcoholic solution of rosolic acid and then with strong soda solution; cotton is discoloured.

**13. Quantitative Estimation of Silk, Wool and Cotton.**—Zinc chloride solution (Rémont). The purified fibre (about 2 grammes), freed from dye, is

(a) Placed in a boiling solution of basic zinc chloride (sp. gr. 1.69 to 1.70), left fifteen minutes on the water-bath and washed until the washings no longer contain zinc. The silk is dissolved, its amount is estimated by the loss in weight. The zinc chloride solution is obtained by heating together 1,000 parts of zinc chloride, 850 parts of water and 40 parts of zinc oxide until solution is complete.

(b) A further quantity of 2 grammes is immersed in 60 to 80 c.c. of caustic soda solution (1.5 per cent.), which is gently boiled for fifteen minutes, the fibre is carefully washed, dried and weighed; the loss in weight = wool.

(c) The remainder is vegetable fibre; 5 per cent. must be added, since the original has been somewhat decomposed, and the same amount must be deducted from the percentage of wool.

**14. Detection of Shoddy.**—Artificial wool or shoddy is a mixture of used wool and wool waste with more or less unused wool, used silk, silk waste, flax and cotton. Shoddy is more rapidly swollen and dissolved by alkalis than new wool. The vegetable fibres are estimated according to 13 (b), by removing the woollen fibre. The silk is estimated according to 13 (a), or by means of strong sulphuric acid, in which the silk dissolves rapidly, the wool slowly, the loss in weight = silk. The approximate composition of shoddy can also be well estimated microscopically (see Figs. 3, 4, etc.). Shoddy is distinguished under the microscope by the irregularity and varying diameter (sudden contractions and swellings) of the fibres, the want of scales, the shortness of the individual hairs and difference of colour.

**15. Discrimination between Genuine and Tussur Silk.**—In order to distinguish mulberry silk from the wild or tussur silk, Persoz boils for one minute with a zinc chloride solution of 15 B.; genuine mulberry silk is dissolved, tussur silk is hardly attacked.

**16. Artificial Silk.**—Artificial silk is composed essentially of nitrocellulose, natural silk of albuminous matters.

(a) Chardonnet artificial silk is prepared by nitrating cellulose to the octonitrate, which is then dissolved in ether-alcohol.

(a<sub>1</sub>) Chardonnet coagulates with a mixture of alcohol and water or with dilute sulphuric acid.

(a<sub>2</sub>) Chardonnet removes the danger of inflammability ("denitrates") by means of dilute nitric acid (sp. gr. 1.32), ferrous chloride, ammonium phosphate, etc.

(a<sub>3</sub>) Chardonnet's silk is lustrous, pliable and possesses the peculiar "feel" of boiled-off silk.

(b) Du Vivier dissolves trinitrocellulose in glacial acetic acid.

(b<sub>1</sub>) Du Vivier uses a secret fluid.

(b<sub>2</sub>) Du Vivier denitrates by the addition of 20 per cent. of



fish glue and 10 per cent. of guttapercha, followed by a complicated treatment.

(*b*<sub>3</sub>) Du Vivier's silk is more brittle, but very white and more lustrous than natural silk.

(*c*) Lehner dissolves nitrocellulose in methyl alcohol-ether or ether-sulphuric acid, and adds natural silk waste, dissolved in glacial acetic acid.

(*c*<sub>1</sub>) Lehner coagulates with a mixture of turpentine oil, chloroform and oil of juniper.

(*c*<sub>2</sub>) Lehner dilutes with fire-proofing salts such as sodium acetate, etc.

(*c*<sub>3</sub>) Lehner's silk has only just recently been brought into commerce.

### 17. Differences between Artificial and Natural Silk.—

The artificial silks can be distinguished from natural silk by means of the following reactions:—

(*a*) Artificial silk dissolves in alkalis with a yellow, natural silk with a white colour.

(*b*) Artificial silk is insoluble in an alkaline copper solution containing glycerin, in which natural silk dissolves at the ordinary temperature. Ten grammes of copper sulphate are dissolved in 100 c.c. of water and 5 grammes of pure glycerin added, caustic alkali is then added until the precipitate redissolves. This solution not only renders possible the detection of artificial silk, but also a complete separation and quantitative estimation of artificial silk in mixtures with natural silk.

(*c*) Artificial silk gives the nitric acid reaction with diphenylamine and brucine, natural silk does not (*Chem. News*, 1897, 2, 121).

### REAGENTS FOR THE SYSTEMATIC EXAMINATION OF TEXTILE FIBRES.

18. Aniline sulphate, in 1 per cent. aqueous solution, colours lignified cells, according to the extent of lignification, pale yellow to golden yellow.

19. Phloroglucinol, in 0.5 per cent. aqueous solution, indicates lignified cells by a slight reddish to a deep red

coloration, when the fibre has been previously moistened with hydrochloric acid.

20. Iodine with sulphuric acid. Two scales of iodine are moistened in a flask with 5 to 6 drops of alcohol, and then so much water added that a slightly wine-yellow solution remains. The object to be examined is moistened with dilute sulphuric acid (1. 2) and then with the iodine solution, or *vice versa*.

21. A 5 per cent. alcoholic solution of magenta.

22. A 5 per cent. aqueous solution of lead acetate.

23. Saturated aqueous solution of picric acid.

24. Basic zinc chloride solution as 13 (a).

By means of these reagents the following course of examination, recommended by Pinchon, is conducted :—

|   |                      |  |   |                                   |
|---|----------------------|--|---|-----------------------------------|
| 10 per cent. solution of caustic soda or potash | All dissolves.       | Zinc chloride (24 or 13(a)) dissolves all in the cold.     | The solution is <i>not</i> blackened on the addition of lead acetate, 22.   | SILK.                             |
|   |                      | Zinc chloride dissolves partially                          | The soluble part is not blackened by 22. The insoluble part is turned brown or black by 22.   | SILK and WOOL.                    |
|   |                      | Zinc chloride dissolves nothing.                           | The mass is blackened by lead acetate, 22.  | WOOL.                             |
|   | Remains undissolved. | Chlorine water or ammonia colours the fibre reddish brown. | Fibre coloured red by nitric acid.  | NEW ZEALAND HEMP.                 |
|   |                      | Chlorine water or ammonia does not colour the fibre.       | 21 colours the fibre permanently. 20 colours it yellow.   | HEMP.                             |
|   |                      | Chlorine water or ammonia does not colour the fibre.       | Caustic potash colours the fibre yellow. The coloration by 21 is not permanent, but can be washed out. Caustic potash does not colour the fibre yellow. | FLAX. COTTON.                     |
|   | Dissolves partially. | 24 dissolves a portion.                                    | Caustic potash partially dissolves the portion insoluble in 24; the residual fibres dissolve in ammoniacal copper oxide, 4.                             | Mixture of WOOL, SILK and COTTON. |
|   |                      | 22 colours nothing.  | 22 colours a portion yellow, the rest remains white.  | SILK and COTTON.                  |
|   |                      | 24 dissolves nothing.                                      | Nitric acid colours a portion yellow, the rest remains white.   | WOOL and COTTON.                  |

In addition to the chemical examination of the textile fibres, which now are numbered by hundreds, microscopic examination is not to be neglected. The advantage of the latter is that the fibre, whether dyed or not, generally does not require the treatment which is a necessary preliminary to the chemical examination—removal of dressing and dye. It is sufficient to moisten the single, well-isolated fibre with glycerin or water, or to prepare sections of it, and at once to examine under the microscope. On the other hand, a certain amount of practice is requisite; a course of examination of the known fibres must be followed, and their characteristics learnt. However, without any great amount of practice, it is possible to recognise at least the more important fibres, by making use of a proper collection of sample of fibres for comparison.

The specific characters of the best known fibres are as follows:—

*Wool.*—The wool fibre is cylindrical but extremely rough, being composed of a large number of modified epithelial scales (skin cells) which are arranged overlapping each other like tiles. There is a very marked central cavity which is more or less coloured with pigment. The length of individual fibres varies very considerably, from 2·5 to 23 centimetres according to whether it is short or long “staple”. The diameter of the fibre is also variable according to the breed of the sheep from which it is taken, being 0·07 to 0·5 mm. Wool is highly nitrogenous, as may be inferred from the way in which it burns. It contains in its pure state (Hummell):—

|          |         |                 |
|----------|---------|-----------------|
| Carbon   | . . . . | 49·25 per cent. |
| Hydrogen | . . . . | 7·57 “          |
| Oxygen   | . . . . | 23·66 “         |
| Nitrogen | . . . . | 15·86 “         |
| Sulphur  | . . . . | 3·66 “          |
|          |         | <hr/>           |
|          |         | 100·00          |

The wool as removed from the sheep is, however, never pure, containing more or less “suint” or wool fat (impure cholesterin and potash salts) and dirt which are removed

from it by washing previous to spinning. The wool washing waters are subsequently treated with acid for the recovery of the wool fat and fatty acids which constitute the valuable material known as "Yorkshire Grease".

**Silk.**—Like wool, silk is a nitrogenous material, but it differs very considerably from the former in its appearance and properties. It is a continuous fibre formed as a covering to its cocoon by the caterpillar of the silk moth (*Bombyx mori*), issuing as a liquid from a circular opening in the body of the insect and quickly drying, it is a perfectly cylindrical fibre, of 350 to 1250 metres length and uniform diameter of about 0.018 mm. It is striated, has no central canal and has a very high lustre. Silk fibre consists principally of three substances, silk fibre or fibroin, constituting about 53 per cent. of the fibre, with about 20 per cent. of silk gelatine, 25 per cent. of albuminous material, and small quantities of wax, resinous and colouring matters. During washing the silk gelatine is more or less removed.

**Cotton.**—The cotton fibre is obtained from the seeds of the cotton plant, *Gossypium barbadense*, etc., and consists of a flattened, tape-like fibre with thickened edges. Individual fibres vary in length according to the locality in which it is grown, from 2.5 to 6 c.m. and in diameter from .017 to .05 mm. It consists almost entirely of cellulose ( $C_6H_{10}O_5$ ) with traces only of wax and gummy matters.

**Flax or Linen.** Flax is the product of the linseed plant (*Linum usitatissimum*). It differs from cotton in having a high lustre when in its finished condition. The fibres are thick walled and the central cavity is very much smaller than in cotton, besides which it is not continuous, there being nodes at intervals resembling bamboo. The fibre varies in length from 25 to 30 mm. and in breadth from .02 to .025 mm. Bleached linen consists essentially of cellulose, but in the unbleached state it contains large quantities of other constituents of a woody type.

**China Grass or Ramie.**—In its appearance this fibre resembles linen, but it is even more lustrous and exceedingly strong. It is obtained from a fibrous plant, *Bolmeria*

*nivea*, and consists of long cellular tissue which varies in diameter at different parts of the fibre.

**Jute.**—Jute is a woody fibre obtained from *Corchorus olitorius*, etc. It is somewhat lustrous, but usually of a yellow colour as it is very difficult to bleach without destruction of the fibre. The fibres resemble those of flax to some extent and have a central cavity. There is usually more or less brownish lignin attached to the fibres.

**Hemp** is the product of *Cannabis sativa*. It is a woody fibre resembling jute, but much coarser.

**Artificial Silks.**—There are three varieties of artificial silk, those made from nitrocellulose, those produced from viscose and those produced from cuprocellulose solution. They resemble each other in appearance, being continuous cylindrical fibres, striated, extremely lustrous, and of even diameter. The diameter varies with the size of openings in the tubes used in the spinnarets of the machine and also on the strength of the solution employed. Viscose fibres examined were .0014 to .00168 mm. and cuprocellulose .00042 to .00084 in.

## CHAPTER III.

### INORGANIC MATERIALS.

#### HYDROCHLORIC ACID.

THE strength of hydrochloric acid may be estimated by means of a determination of the specific gravity, or better—since a small proportion of sulphuric acid increases the density considerably—by volumetric processes. Fifty grammes are diluted to 1,000 c.c. and 100 c.c. titrated with normal caustic soda; 1 c.c. of normal soda = 0.0364 gramme of hydrochloric acid.

When other acids (sulphuric) are not to be determined as hydrochloric acid, the proportion of pure hydrochloric acid, or hydrochloric acid + chlorides, may be determined by Volhard's process: 20 to 25 grammes of the acid are diluted to 1,000 c.c., excess of  $\frac{1}{10}$  N silver solution is added to 20 or 25 c.c. of the dilute acid, after adding nitric acid and a few c.c. of a strong solution of iron alum. The excess of silver is titrated by  $\frac{1}{10}$  N ammonium sulphocyanide solution. As soon as all the silver is precipitated as sulphocyanide, the reaction between the sulphocyanide and iron alum occurs, and is recognised by the brownish coloration. The volume of silver solution added, minus the sulphocyanide solution used, gives the number of c.c. of silver nitrate solution required to combine with the chlorine. 1 c.c. of  $\frac{1}{10}$  N silver solution = 0.00354 gramme of Cl = 0.00364 gramme of HCl. If chlorides be present in addition to the free acid, they must be estimated, in the residue left on evaporation, by means of silver nitrate and potassium chromate and the amount of hydrochloric acid found must be deducted from the total. The difference between total

acid (as found by titration with caustic soda) and hydrochloric acid represents the foreign acids. A similar process, when the total acids are required, is as follows: the hydrochloric acid solution, after titration with caustic soda, which is now a neutral chloride solution, is titrated directly with silver nitrate and potassium chromate. One c.c. of  $\frac{1}{10}$  N silver solution = 0.00364 gramme of HCl. It should not be necessary to state that the whole volume of hydrochloric acid neutralised by soda is not titrated by silver nitrate, but, since decinormal silver solution is used, an aliquot part of the liquid only is titrated, or a smaller quantity of hydrochloric acid is taken specially for this purpose.

The presence of free chlorine and nitric acid is detected by means of diphenylamine (which see), free chlorine also by its bleaching action on litmus paper. Other impurities are principally sulphuric acid, iron, arsenic, other heavy metals, alkali salts, etc.; a portion of the acid is evaporated, the residue should not be more than a trace. The acid should not contain much sulphuric acid, in the case of crude hydrochloric acid it should not exceed 1 per cent. (may be estimated by precipitation with barium chloride). For many purposes only a very small quantity of iron is permissible; acid for bleaching may not contain more than 0.03 per cent. (test with potassium sulphocyanide). The iron may conveniently be estimated colorimetrically (see under *Water*) or also gravimetrically and volumetrically (see *Iron Salts*).

*Applications.*—Generally speaking, less used than sulphuric acid, since it always bleaches to some extent, if it contains or produces free chlorine. In bleaching, to “sour” the goods (for this purpose it should not contain more than 0.03 per cent. of iron); to decompose the bleaching powder after bleaching (for this purpose it must be absolutely free from iron); in bleaching with barium peroxide; in aniline black dyeing as aniline hydrochloride (cotton, mixtures of cotton with wool and silk, and recently, experimentally, wool); in blue printing; to remove lime after passing through substances containing lime; in carbonising woollen rags (shoddy); in the manufacture of bleaching powder; in

black silk dyeing (also wool-dyeing); in grounding with Prussian blue, etc.

• *Specific Gravity and Strength of Hydrochloric Acid (Kolb).*

| °B.  | Specific Gravity. | At 0° C. 100 parts contain HCl. | At 15° C. 100 parts contain parts of |                |                |                |
|------|-------------------|---------------------------------|--------------------------------------|----------------|----------------|----------------|
|      |                   |                                 | HCl.                                 | Acid of 20° B. | Acid of 21° B. | Acid of 22° B. |
| 0    | 1.000             | 0.0                             | 0.1                                  | 0.3            | 0.3            | 0.3            |
| 1    | 1.007             | 1.4                             | 1.5                                  | 4.7            | 4.4            | 4.2            |
| 2    | 1.014             | 2.7                             | 2.9                                  | 9.0            | 8.6            | 8.1            |
| 3    | 1.022             | 4.2                             | 4.5                                  | 14.1           | 13.3           | 12.6           |
| 4    | 1.029             | 5.5                             | 5.8                                  | 18.1           | 17.1           | 16.2           |
| 5    | 1.036             | 6.9                             | 7.3                                  | 22.8           | 21.5           | 20.4           |
| 6    | 1.044             | 8.1                             | 8.9                                  | 27.8           | 26.2           | 24.4           |
| 7    | 1.052             | 9.9                             | 10.4                                 | 32.6           | 30.7           | 29.1           |
| 8    | 1.060             | 11.4                            | 12.0                                 | 37.6           | 35.4           | 33.6           |
| 9    | 1.067             | 12.7                            | 13.1                                 | 41.9           | 39.5           | 37.5           |
| 10   | 1.075             | 14.2                            | 15.0                                 | 46.9           | 44.2           | 42.0           |
| 11   | 1.083             | 15.7                            | 16.5                                 | 51.6           | 48.7           | 46.2           |
| 12   | 1.091             | 17.2                            | 18.1                                 | 56.7           | 53.4           | 50.7           |
| 13   | 1.100             | 18.9                            | 19.9                                 | 62.3           | 58.7           | 55.7           |
| 14   | 1.108             | 20.1                            | 21.5                                 | 67.3           | 63.1           | 60.2           |
| 15   | 1.116             | 21.9                            | 23.1                                 | 72.3           | 68.1           | 64.7           |
| 16   | 1.125             | 23.6                            | 24.8                                 | 77.6           | 73.2           | 69.4           |
| 17   | 1.134             | 25.2                            | 26.6                                 | 83.3           | 78.5           | 74.5           |
| 18   | 1.143             | 27.0                            | 28.4                                 | 88.9           | 83.0           | 79.5           |
| 19   | 1.152             | 28.7                            | 30.2                                 | 94.5           | 89.0           | 84.6           |
| 19.5 | 1.157             | 29.7                            | 31.2                                 | 97.7           | 92.0           | 87.1           |
| 20   | 1.161             | 30.4                            | 32.0                                 | 100.0          | 94.4           | 89.6           |
| 20.5 | 1.166             | 31.4                            | 33.0                                 | 103.3          | 97.3           | 92.1           |
| 21   | 1.171             | 32.3                            | 33.9                                 | 106.1          | 100.0          | 94.9           |
| 21.5 | 1.175             | 33.0                            | 34.7                                 | 10.6           | 102.4          | 97.2           |
| 22   | 1.180             | 34.1                            | 35.7                                 | 111.7          | 105.3          | 100.0          |
| 22.5 | 1.185             | 35.1                            | 36.8                                 | 115.2          | 108.6          | 103.0          |
| 23   | 1.190             | 36.1                            | 37.9                                 | 118.6          | 111.8          | 106.1          |
| 23.5 | 1.195             | 37.1                            | 39.0                                 | 122.0          | 115.6          | 109.2          |
| 24   | 1.199             | 38.0                            | 39.8                                 | 124.6          | 117.4          | 111.4          |
| 24.5 | 1.205             | 39.1                            | 41.2                                 | 130.0          | 121.5          | 115.4          |
| 25   | 1.210             | 40.2                            | 42.4                                 | 132.7          | 125.0          | 119.0          |
| 25.5 | 1.212             | 41.7                            | 42.9                                 | 134.3          | 126.6          | 120.1          |

• *CHLORIDES.*

The chlorides of the alkalis and alkaline earths are required to dissolve to a clear solution, have a neutral re-



action, be dry and free from foreign metals. Thus, according to circumstances, the solubility, proportion of water and the presence of foreign acids and metals will be investigated. In a detailed examination the halogen and metal may both be estimated. As an example, see the analysis of stannic chloride. In neutral salts the hydrochloric acid may be estimated by means of silver solution, using neutral potassium chromate,  $K_2CrO_4$ , as indicator (see *Water and Hydrochloric Acid*). Several of the more important chlorides are specially mentioned in the following pages.

**Sodium Chloride, Common Salt,**  $NaCl$  = mol. wt. 58.5; solubility in cold water = 35:100, in hot water = 39.5:100.

*Applications.*—Little used in the textile industries; is added to the bath in dyeing with azo dyestuffs; as a dressing. For the latter purpose it is to be used with caution, since almost all dyes are injured by it, and the common qualities being hygroscopic, owing to presence of magnesium chloride, it gives rise to the formation of "mould spots".

**Magnesium Chloride,**  $MgCl_2 \cdot 6H_2O$  = mol. wt. 203.2; solubility, cold water = 150:100; hot water = 367:100.

*Applications.*—It is principally used as a deliquescent for sizing purposes. However, it should not be used in too large quantities (not more than about 100 grammes per litre), since in the succeeding operations, in singeing in the finishing cylinder, etc., decompositions may occur ( $MgCl_2 + H_2O = MgO + 2HCl$ ) and the material be made rotten. In spite of this, 600 to 700 grammes per kilo. are frequently employed.

For convenience a solution of magnesium chloride of 50° Tw. (sp. gr. 1.25) containing 24 per cent. of the salt is usually employed.

**Ammonium Chloride, Sal Ammoniac,**  $NH_4Cl$  = mol. wt. 53.47; solubility, cold water = 37:100; hot water = 100:100.

This salt should leave only a slight residue on ignition, it should not contain too much water, iron or lime. It is not much used, but is sometimes employed as an addition to printing colours, and in aniline black dyeing as a carrier of moisture in order to accelerate the oxidation.

**Barium Chloride**,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  = mol. wt. 244.36; solubility, cold water = 38.4 : 100; hot water = 78.1 : 100.

By passing through a solution of this salt and then through sulphate of soda solution, large quantities of barium sulphate can be precipitated in the fabric (flannel); this application is restricted owing to the poisonous nature of the compound, in any case the sulphate should be in excess. It has also been proposed as a water purifier (see *Water*).

**Zinc Chloride**,  $\text{ZnCl}_2$  = mol. wt. 136.29; solubility, cold water = 300 : 100; hot water, melts.

*Applications.*—Used as a mordant for Water Blue and as a double salt of certain commercial dyes (green, methylene blue, etc.). In the manufacture of lakes it is used together with tin, alumina and iron (lakes of the ponceaux, eosines, etc.), also it is added in small quantities (5 to 10 grammes, 1,000) to size mixings, as a preservative, to prevent the formation of mould.

For convenience it is usually employed in the form of a solution of 100 Tw. (sp. gr. 1.50) containing 35 per cent. of the salt.

**Copper Chloride**,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  = mol. wt. 170.5; solubility, cold water = 60 : 100; hot water melts.

Copper and ferrous sulphates are the principal impurities (examination similar to that of copper sulphate, which see). It may be used as a good oxidising agent in place of copper sulphate and sulphide (aniline, catechu).

**Manganous Chloride**,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  = .97.8; solubility, cold water = 150 : 100; hot water = 650 : 100.

This compound has a restricted application in printing certain fashionable colours and as a fixing agent for catechu; also used in the preparation of manganese bistr.

**Aluminium Chloride**,  $\text{Al}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ ; solubility, cold water = 4 : 1; melts on heating.

Also occurs commercially as a solution of 20° to 30° B. ("Chloralum"). Its principal application is in carbonising wool (in the better class of goods used at a strength of 3° to 6° B.); also for certain special purposes, *e.g.*, when cotton and wool are woven together and the cotton then removed by carbonisation, so that the skeleton of wool remains.

**Stannous Chloride, Tin Crystals, Tin Salt,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ;** solubility, 'cold water = 271; 100 (with partial decomposition turbid liquid); hot water decomposes it.

This important salt often comes into commerce chemically pure; it is, however, sometimes adulterated with magnesium sulphate—since the two salts are similar in appearance—also with zinc chloride and sulphate.

Stannous chloride should be analysed quantitatively. There is no really simple method; the tin and chlorine may be estimated gravimetrically and the actual stannous chloride volumetrically. All the volumetric processes are based upon the reducing properties of stannous chloride.

*Total Tin.*—20 grammes of tin crystals are dissolved in 500 c.c. of water acidified with sulphuric acid; in 25 c.c. of the solution the tin is precipitated by sulphuretted hydrogen, the precipitate dried, roasted to stannic oxide with the proper precautions (Fresenius, *Quant. Anal.*, I. 280), weighed, and calculated to metallic tin or stannous chloride; 150.7 parts of  $\text{SnO}_2 = 118.7$  parts of  $\text{Sn} = 225.62$  parts of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ .

*Stannous Chloride.*—(a) A second 25 c.c. of the solution are titrated by  $\frac{1}{5}$  N permanganate after the addition of ferric chloride free from ferrous salt. Stannic chloride and an equivalent quantity of ferrous chloride are formed, the latter being then oxidised by the permanganate to ferric chloride. Boiled water, free from oxygen, must be used (see Fresenius, *Quant. Anal.*, I. 280). 1 c.c. of  $\frac{1}{5}$  N potassium permanganate = 0.02256 gramme of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ .

(b) To 10 c.c. of the solution 50 c.c. of a 10 per cent. solution of Rochelle salt and 50 c.c. of a 10 per cent. solution of sodium bicarbonate are added, and the mixture titrated with  $\frac{1}{10}$  N iodine solution, using starch solution as indicator. 1 c.c. of  $\frac{1}{10}$  N iodine = 0.01128 gramme of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ .

*Total and Free Acid.*—(a) According to Knecht, Rawson and Löwenthal, the total acid may be determined by immediate titration of the solution (20 c.c.) with normal alkali and phenolphthaleïn (methyl orange is better). The separated stannous hydroxide is said not to affect the titration.

(b) The acid may be determined more accurately as under *Stannic Chloride* (a) and (b).

From the amount of tin found the combined acid is calculated, an excess corresponds to free acid, a deficit to basic chloride.

*Qualitative Examination.*—Pure stannous chloride is soluble in 5 parts of absolute alcohol, almost all impurities and basic salt remaining undissolved. By this means salts of magnesium, zinc, copper and lead, common salt, Glauber's salt, etc., may be found; also an idea is obtained of the proportion of basic chloride, which forms very readily on long keeping:  $3\text{SnCl}_2 + \text{O} + \text{H}_2\text{O} = 2\text{Sn}(\text{OH})\text{Cl} + \text{SnCl}_4$ . The clearer the solution of the salt in alcohol or water, the less basic salt it contains. A commercial product cannot be required to give a completely clear solution.

*Applications.*—Stannous chloride finds extended use in the following operations: in dyeing wool with flavine and cochineal (to  $7\frac{1}{2}$  to 10 per cent. of cochineal, about 3 to 5 per cent. of stannous chloride, with a little tartar, and perhaps also oxalic acid; oxalic acid shades towards yellow, stannous chloride towards blue, cochineal giving a red); in silk-dyeing as a mordant and as fixing agent for catechu; also to make dyes fast to water ( $\text{SnCl}_2$  was formerly used together with  $\text{SnCl}_4$ ); in calico-printing as a discharging agent, since it reduces and destroys the azo dyestuffs, it is also the raw material from which other tin compounds are prepared, *e.g.*, tin acetate.

**Stannic Chloride, Tin Perchloride,  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$**  = mol. wt. 350.5. Melts on heating and is very soluble in water; decomposed by much water; contains 33.7 per cent. of tin.

In an exhaustive examination the following estimations are requisite, in order to obtain a complete knowledge of the composition of the substance: total tin, total acid calculated as chlorine, stannous chloride and stannic chloride, foreign acids (sulphuric and nitric), free chlorine, ammonia, alkali salts and foreign metals, metastannic acid.

*Total Tin.*—25 to 30 grammes of stannic chloride are dissolved to 1 litre; 50 c.c. of the solution are treated with two drops of bromine water (or iodine) in order to oxidise

any stannous chloride present, the bromine is expelled by boiling, and the tin precipitated by excess of ammonium nitrate or sodium sulphate. In case the stannic chloride is strongly acid, a few drops of ammonia are added until the solution begins to be turbid, when it is boiled with ammonium nitrate or sodium sulphate (about 20 grammes) for ten to fifteen minutes. The precipitate is allowed to settle, the liquid decanted off, the precipitate filtered, well washed (especially if sodium sulphate was used), dried, ignited and weighed as tin dioxide,  $\text{SnO}_2$ . Commercial stannic chloride contains 21.5 to 34 per cent. of tin.

*Total Chlorine* (T. Goldschmidt).--(a) 10 c.c. of liquid stannic chloride are weighed off (or 8 to 9 grammes of the solid salt), and diluted to 100 c.c.; 10 p.c. of the solution are brought into a 100 c.c. flask, diluted with 30 to 40 c.c. of water, and then so much  $\frac{1}{2}$  N soda solution added that 0.05 to 0.15 gramme of  $\text{Na}_2\text{CO}_3$  remains in excess; the liquid is then made up to 100 c.c., well shaken and filtered. (In the case of stannic chloride of about 50° B., 42 c.c. of  $\frac{1}{2}$  N soda solution are taken; with solid stannic chloride the necessary quantity of soda solution is calculated from the percentage of tin.) It is absolutely necessary that the soda should be used in such quantity that the excess is at the above degree of dilution, with a larger excess the tin is again partially dissolved and would then be calculated as chlorine; 50 c.c. of the filtrate are now titrated with methyl orange and N or  $\frac{1}{5}$  N or  $\frac{1}{10}$  N hydrochloric or sulphuric acid; the excess of soda, and thence the soda used, is calculated. If litmus or phenolphthalein is used, 10 c.c. of  $\frac{1}{2}$  N hydrochloric acid are added to 50 c.c. of the filtrate, the liquid is boiled for five minutes, allowed to cool and titrated. The volume of soda solution used is calculated to chlorine.

*Basicity*.—The deficiency or excess of chlorine is calculated from the percentages of tin and acid. If there is a deficiency of chlorine, basic salts (tin oxychloride) or stannous chloride (see below) are present; if the chlorine is in excess, free acid is present. The best stannic chloride contains tin and chlorine in exactly equivalent proportions (1Sn to 4Cl).

Example: 10 c.c. of stannic chloride weighed 16.000 grammes. The gravimetric analysis gave 24.25 per cent. of tin, which corresponds to 28.98 per cent. of chlorine. In the experiment 42 c.c. of  $\frac{1}{10}$  N soda solution were used; 3.85 c.c. of decinormal acid were required in titrating back. Now  $14 - (0.385 \times 2) = 13.23$  c.c. of N soda were used;  $13.23 \times 0.03546 = 0.469136 = 0.47$  nearly;  $100 - 0.47 = 100 - x$ , then  $x = 29.37$  per cent. of chlorine, or rather total acid calculated as chlorine. Accordingly there is an excess of chlorine of  $29.37 - 28.98 = 0.39$  per cent., which may be present as free hydrochloric acid.

(b) The following method is much simpler and more rapid, whilst it is not less accurate than the preceding. 25 c.c. of stannic chloride solution (or 15 to 20 grammes of the solid salt) are dissolved to 250 c.c., 25 c.c. of this solution are mixed in a beaker with hot distilled water, oxidised with one drop of bromine water, and the turbid liquid kept almost at the boiling point on the water-bath for about ten minutes longer. The stannic chloride is quantitatively decomposed into stannic hydroxide and free hydrochloric acid, even though it contains a considerable quantity of free acid. The stannic hydroxide is collected on an ashless filter, washed with hot water until the filtrate is neutral, the precipitate dried, the paper burnt, the whole ignited and weighed as  $\text{SnO}_2$ . The filtrate is titrated with N caustic soda and phenolphthalein, 1 c.c. = 0.03546 gramme of chlorine. The weight of tin dioxide multiplied by 0.7876 gives the weight of metallic tin; the weight of the tin or its percentage, multiplied by 1.195, gives the quantity of chlorine required to form  $\text{SnCl}_4$ . This method is very exact and deserves preference over the preceding.

1 gramme  $\text{SnO}_2 = 0.7876$  gramme Sn =  $0.7376 \times 1.195$  gramme Cl, which is required to saturate the tin. The difference between the chlorine found and calculated gives the excess or deficiency of chlorine (see above).

(c) The estimation of the free acid by immediate titration of the stannic chloride with normal caustic soda according to Knecht, Rawson and Lowenthal is quite inaccurate and useless; the method of Silbermann (*Färberzeit.*, 1897, No. 5) is equally tedious and inaccurate.

The total acid may, however, be approximately estimated by direct titration of the solution of the salt with normal caustic soda and methyl orange as indicator (*not* phenolphthaleïn).

*Stannous Chloride*.—Qualitatively by means of mercuric chloride. Quantitatively by means of iodine or permanganate (see *Stannous Chloride*).

*Nitric Acid, Free Chlorine and Ammonia* are generally only present in slight traces. They are usually only sought qualitatively, but may be estimated colorimetrically. It must not be forgotten that ferric chloride gives the reaction with potassium iodide starch paper. Nitric acid may be estimated by means of indigo solution, exactly as in water (see *Water and Nitric Acid*).

*Sulphates* of sodium and iron are occasionally fraudulently added in order to increase the specific gravity. If the sulphuric acid reaction indicates more than traces, the sulphates may be estimated directly by precipitation with barium chloride, or indirectly by evaporating and igniting an aliquot part of the filtrate from the tin (precipitated by ammonium nitrate), the result is then given as "metals not tin". A small quantity of iron must be allowed.

*Metastannic Acid* is obtained as the portion insoluble in excess of caustic soda solution.

*Total Chlorine*.—The estimation of the total chlorine is void of special interest, since the chlorides of the alkalis, etc., would have been found already amongst the "metals not tin". In the event of an estimation being required, the tin is first precipitated, and then the chlorine from the filtrate by means of silver nitrate, otherwise tin would be precipitated along with the silver chloride.

*Requirements of Stannic Chloride*.—It must contain as much pure  $\text{SnCl}_4$  as possible, *i.e.*, contain chlorine equivalent to the tin, not too much free acid (up to 0.5 per cent.) and not too much basic salt (deficiency of chlorine not more than 1 per cent.) and tin oxychloride; further, as little as possible of metastannic acid, nitric acid, free chlorine, sulphates, salts of iron and the alkalis. Stannic chloride is now made on the large scale of a quality to satisfy every

requirement, and technical inconveniences now occur more rarely than before its introduction.

*Applications.*—Formerly occurred in commerce as “pink salt,” a double compound of stannic and ammonium chlorides, now as pure stannic chloride. For brightening (60° grammes soap, 3 grammes stannic chloride, 5 grammes crystallised soda, 20 grammes olive oil, boil well for ten minutes, and make up to 1,000 grammes; if the mixture acquires a brown colour it is useless). in wool-dyeing (alizarine with or without alum); as a cotton mordant (soap 5° to 10: 1,000;  $\text{SnCl}_4$  of 4° B., aluminium acetate of 7° B. or sodium stannate with neutralised alum); in dyeing with ponceaux; in dyeing wool red (however makes the fibre hard); in particular as the silk weighting material *par excellence* (27° to 30° B.), this application has acquired great importance during the last twelve years.

*Percentage of Tin and Specific Gravity.*

| Specific Gravity<br>°B. | Tin per cent. | Specific Gravity<br>°B. | Tin per cent. | Specific Gravity<br>°B. | Tin per cent. |
|-------------------------|---------------|-------------------------|---------------|-------------------------|---------------|
| 3                       | 1             | 19                      | 8.0           | 35                      | 15.4          |
| 5                       | 2             | 21                      | 8.7           | 37                      | 16.0          |
| 7                       | 3             | 23                      | 9.5           | 38                      | 16.3          |
| 9                       | 3.7           | 25                      | 10.7          | 39                      | 16.7          |
| 11                      | 4.6           | 27                      | 11.5          | 40                      | 17.2          |
| 13                      | 5.3           | 29                      | 12.5          | 50                      | 21.6          |
| 15                      | 6.2           | 31                      | 13.4          | 55                      | 24.0          |
| 17                      | 7.3           | 33                      | 14.5          | 60                      | 26.0          |

“Tin Spirits” contain stannous and stannic chlorides, with or without free hydrochloric and sulphuric acids, and vary in composition to an extraordinary degree. The chlorides of tin are estimated by the methods already described; the free acids are also to be determined.

In addition to stannous and stannic chlorides, a number of other preparations of tin come into the market, in which nitric and sulphuric acids, in addition to hydrochloric acid,



have been used as solvents. Either stannous or stannic chloride may predominate in these solutions. The nitric acid may be estimated by titration with indigo solution (see *Water*), in which case the tin should first be precipitated. For the most part, these preparations are falling into disuse, being replaced by the pure compounds or by mixtures of these made by the consumer. The following are the formulae for certain solutions of this type: "Nitro-chloride of tin," "Physic bath" or "Composition" = 5 kilos. of nitric acid + 5 kilos. of stannous chloride; "Scarlet Composition" = 5 kilos. of tin + 6 kilos. of nitric acid + 18 kilos. of hydrochloric acid + 6 litres of water; "Nitrate of tin" = 5 kilos. of tin + 20 kilos. of hydrochloric acid + 10 kilos. of nitric acid; "Sulphate of tin" = 5 kilos. of tin + 9 kilos. of hydrochloric acid + 2 kilos. of sulphuric acid + 2 litres of water, etc.

*Application* restricted, otherwise as given under *Stannous* and *Stannic Chlorides*, but not used for weighting silk.

**Chromium Chloride**,  $\text{Cr}_2\text{Cl}_6$  = mol. wt. 316.7. Commercially as a solution of 30° B., etc.

The percentage of chromium gives the value of the substance. It is estimated by precipitation with ammonia and ignition to  $\text{Cr}_2\text{O}_3$ . When much iron is present, which at times is the case, a determination should be made (Fresenius, *Quant. Anal.*, I. 442). The solution should not be strongly acid, but should not be basic or contain much sulphuric acid.

*Application*.—As a mordant on cotton and silk, for adjectival colouring matters and especially for alizarine. It deposits the chromic oxide more readily upon the fibre than, e.g., chromic alum (which see); also in calico-printing in order to produce the lake of the colouring matter.

#### FLUORIDES AND BIFLUORIDES.

Recently fluorides have come into use in the textile industries alongside the chlorides, though such use is at present partially experimental. Free hydrofluoric acid is not employed, although it is stated, in dilute solution, to impart a greater lustre to silk.

**Alkaline Bifluorides**,  $\text{KF} \cdot \text{HF}$  and  $\text{NaF} \cdot \text{HF}$ . These should not contain too much foreign acid, much iron or other metals.

*Application.*—Used principally to replace cream of tartar and potassium bichromate. Up to the present no particularly favourable or unfavourable results have been recorded; the fabric, however, is made appreciably (1 to 2 per cent.) stronger.

**Chromium Fluoride**,  $\text{Cr}_2\text{F}_6 \cdot 8\text{H}_2\text{O}$  = mol. wt. 362. This salt should contain about 42 to 43 per cent. of chromium oxide, should not be too acid and should be as far as possible free from iron, which metal may be estimated as in chromium chloride.

*Application.*—In calico-printing instead of chromium acetate, with which, however, it cannot compete; in mordanting wool instead of potassium bichromate, which is the chief application. The chromium fluoride black so obtained is said not to turn green, whilst potassium bichromate black fades towards green. It should, however, not be used in copper vessels, since copper fluoride is formed, which weakens the fibre. Wooden vessels with lead coils must be used, or, according to Kertész, if zinc strips be hung in copper vessels, the copper remains unattacked.

**Chromium Oxyfluoride**, or basic fluoride chromium fluoride + chromium oxide. The percentage of chromium and the basicity are to be estimated as for ferric sulphate (which see).

*Application.*—As chromium fluoride.

**Copper Fluoride** has been recommended as an oxidising agent for aniline black, and for the after-oxidation; hitherto it has been little used.

**Antimony Fluoride** and **Aniline Hydrofluoride** have been recommended, but never introduced. The latter is especially recommended for aniline black on silk.

**Antimony Fluoride Double Salts.** Antimony salt,  $\text{SbF}_3 \cdot (\text{NH}_4)_2\text{SO}_4$ , contains 47 per cent. of  $\text{Sb}_2\text{O}_3$ . Double antimony fluoride,  $\text{SbF}_3 \cdot \text{NaF}$ , contains 66 per cent. of  $\text{Sb}_2\text{O}_3$ . These compounds are offered as substitutes for tartar emetic. Before use a trace of soda should be added, in order to ac-

celerate the formation of the lake (the colour then, however, rubs off more readily).

In printing, 2 to 5 grammes of antimony salt are added per kilo. of colour, and soda is added to the extent of  $\frac{1}{2}$  to  $\frac{1}{6}$  of the weight of the antimony salt.

#### SULPHURIC ACID.

$\text{H}_2\text{SO}_4 = 98$ ; soluble in water in every proportion.

The strength is estimated from the specific gravity, or volumetrically, as with hydrochloric acid: 25 grammes are diluted to 1,000 c.c., 50 c.c. are taken and titrated with normal caustic soda; 1 c.c. of normal soda = 0.049 gramme of  $\text{H}_2\text{SO}_4 = 0.04$  gramme of  $\text{SO}_3$ . In the case of very strong acid, above 96 per cent., the specific gravity cannot be used (see table), volumetric methods must then be employed, which is, indeed, always desirable when accuracy is required. In addition to the strength, the following impurities may be tested for: sodium sulphate (residue on ignition), gypsum, alumina, iron, lead, arsenic, zinc, copper, hydrochloric, nitric and sulphurous acids. The residue on ignition should not exceed tenths of 1 per cent. Sulphurous acid is detected by means of iodine (see *Fuming Sulphuric Acid* and *Sulphites*).

The determinations of Kolb are unreliable for sulphuric acid containing more than 90 per cent. of  $\text{H}_2\text{SO}_4$ . The results of Lunge and Naef are given in the table on p. 46, the values marked \* have been directly observed, the others are obtained by interpolation. These figures relate to *chemically pure* acid; the specific gravities of very concentrated commercial acid are higher.

*Application*.—Used on a very large scale. In dyeing wool in the acid bath, silk in acidified “boiled-off liquor” (certain dyes, such as eosine, cannot withstand sulphuric acid, in their case acetic acid must be used); in stripping the colour-lake from the fibre; in carbicising loose wool ( $2^\circ$  to  $5^\circ$  B.); in calico bleaching instead of hydrochloric acid, which often contains iron and free chlorine; in discharging indigo; in calico-printing to remove resists; in the preparation of

*Specific Gravity of Sulphuric Acid at 15° C. (Kolb).*

| °R. | Specific Gravity. | 100 parts by weight contain  |   |                                |                                | 1 litre contains kilose of |                                |                   |                   |
|-----|-------------------|------------------------------|---|--------------------------------|--------------------------------|----------------------------|--------------------------------|-------------------|-------------------|
|     |                   | SO <sub>2</sub><br>per cent. | H <sub>2</sub> SO <sub>4</sub><br>per cent. | Acid of<br>60° R.<br>per cent. | Acid of<br>53° R.<br>per cent. | SO <sub>2</sub>            | H <sub>2</sub> SO <sub>4</sub> | Acid of<br>60° R. | Acid of<br>53° R. |
| 0   | 1.000             | 0.7                          | 0.9   | 1.2                            | 1.3                            | 0.007                      | 0.009                          | 0.012             | 0.013             |
| 1   | 1.007             | 1.5                          | 1.9   | 2.4                            | 2.8                            | 0.015                      | 0.019                          | 0.024             | 0.028             |
| 2   | 1.014             | 2.3                          | 2.8   | 3.6                            | 4.2                            | 0.023                      | 0.028                          | 0.036             | 0.042             |
| 3   | 1.022             | 3.1                          | 3.8   | 4.9                            | 5.7                            | 0.032                      | 0.039                          | 0.050             | 0.058             |
| 4   | 1.029             | 3.9                          | 4.8   | 6.1                            | 7.2                            | 0.040                      | 0.049                          | 0.063             | 0.074             |
| 5   | 1.037             | 4.7                          | 5.8   | 7.4                            | 8.7                            | 0.049                      | 0.060                          | 0.077             | 0.090             |
| 6   | 1.045             | 5.6                          | 6.8   | 8.7                            | 10.2                           | 0.059                      | 0.071                          | 0.091             | 0.107             |
| 7   | 1.052             | 6.4                          | 7.8   | 10.0                           | 11.7                           | 0.067                      | 0.082                          | 0.105             | 0.123             |
| 8   | 1.060             | 7.2                          | 8.8   | 11.3                           | 13.1                           | 0.076                      | 0.093                          | 0.120             | 0.139             |
| 9   | 1.067             | 8.0                          | 9.8   | 12.6                           | 14.6                           | 0.085                      | 0.105                          | 0.134             | 0.156             |
| 10  | 1.075             | 8.8                          | 10.8  | 13.8                           | 16.1                           | 0.095                      | 0.116                          | 0.148             | 0.173             |
| 11  | 1.083             | 9.7                          | 11.9  | 15.2                           | 17.8                           | 0.105                      | 0.129                          | 0.165             | 0.193             |
| 12  | 1.091             | 10.6                         | 13.0  | 16.7                           | 19.4                           | 0.116                      | 0.142                          | 0.182             | 0.211             |
| 13  | 1.100             | 11.5                         | 14.1  | 18.1                           | 21.0                           | 0.126                      | 0.155                          | 0.199             | 0.231             |
| 14  | 1.108             | 12.4                         | 15.2  | 19.5                           | 22.7                           | 0.137                      | 0.168                          | 0.216             | 0.251             |
| 15  | 1.116             | 13.2                         | 16.2  | 20.7                           | 24.2                           | 0.147                      | 0.181                          | 0.231             | 0.270             |
| 16  | 1.125             | 14.1                         | 17.3  | 22.2                           | 25.8                           | 0.159                      | 0.195                          | 0.250             | 0.290             |
| 17  | 1.134             | 15.1                         | 18.5  | 23.7                           | 27.6                           | 0.172                      | 0.210                          | 0.269             | 0.313             |
| 18  | 1.142             | 16.0                         | 19.6  | 25.1                           | 29.2                           | 0.183                      | 0.224                          | 0.287             | 0.333             |
| 19  | 1.152             | 17.0                         | 20.8  | 26.6                           | 31.0                           | 0.196                      | 0.238                          | 0.306             | 0.357             |
| 20  | 1.162             | 18.0                         | 22.2  | 28.4                           | 33.1                           | 0.209                      | 0.258                          | 0.330             | 0.385             |
| 21  | 1.171             | 19.0                         | 23.3  | 29.8                           | 34.8                           | 0.222                      | 0.273                          | 0.349             | 0.407             |
| 22  | 1.180             | 20.0                         | 24.5  | 31.4                           | 36.6                           | 0.236                      | 0.289                          | 0.370             | 0.432             |
| 23  | 1.190             | 21.1                         | 25.8  | 33.0                           | 38.5                           | 0.251                      | 0.307                          | 0.393             | 0.458             |
| 24  | 1.200             | 22.1                         | 27.1  | 34.7                           | 40.5                           | 0.265                      | 0.325                          | 0.416             | 0.486             |
| 25  | 1.210             | 23.2                         | 28.4  | 36.4                           | 42.4                           | 0.281                      | 0.344                          | 0.440             | 0.513             |
| 26  | 1.220             | 24.2                         | 29.6  | 37.9                           | 44.2                           | 0.295                      | 0.361                          | 0.465             | 0.539             |
| 27  | 1.231             | 25.3                         | 31.0  | 39.7                           | 46.3                           | 0.311                      | 0.382                          | 0.489             | 0.570             |
| 28  | 1.241             | 26.3                         | 32.2  | 41.2                           | 48.1                           | 0.326                      | 0.400                          | 0.511             | 0.597             |
| 29  | 1.252             | 27.3                         | 33.4  | 42.8                           | 49.9                           | 0.342                      | 0.418                          | 0.536             | 0.625             |
| 30  | 1.263             | 28.3                         | 34.7  | 44.4                           | 51.8                           | 0.357                      | 0.438                          | 0.561             | 0.654             |
| 31  | 1.274             | 29.4                         | 36.0  | 46.1                           | 53.7                           | 0.374                      | 0.459                          | 0.587             | 0.684             |
| 32  | 1.285             | 30.5                         | 37.4  | 47.9                           | 55.8                           | 0.392                      | 0.481                          | 0.616             | 0.717             |
| 33  | 1.297             | 31.7                         | 38.8  | 49.7                           | 57.9                           | 0.411                      | 0.503                          | 0.645             | 0.751             |
| 34  | 1.308             | 32.8                         | 40.2  | 51.1                           | 60.6                           | 0.429                      | 0.526                          | 0.674             | 0.785             |
| 35  | 1.320             | 33.8                         | 41.6  | 53.3                           | 62.2                           | 0.447                      | 0.549                          | 0.704             | 0.820             |
| 36  | 1.332             | 35.1                         | 43.0  | 55.1                           | 64.2                           | 0.468                      | 0.573                          | 0.734             | 0.856             |
| 37  | 1.345             | 36.2                         | 44.4  | 56.9                           | 66.3                           | 0.487                      | 0.597                          | 0.765             | 0.892             |
| 38  | 1.357             | 37.2                         | 45.5  | 58.3                           | 67.9                           | 0.505                      | 0.617                          | 0.791             | 0.921             |
| 39  | 1.370             | 38.3                         | 46.9  | 60.0                           | 70.0                           | 0.525                      | 0.642                          | 0.822             | 0.959             |
| 40  | 1.383             | 39.5                         | 48.3  | 61.9                           | 72.1                           | 0.546                      | 0.668                          | 0.856             | 0.997             |
| 41  | 1.397             | 40.7                         | 49.8  | 63.8                           | 74.8                           | 0.569                      | 0.696                          | 0.891             | 1.038             |
| 42  | 1.410             | 41.8                         | 51.2  | 65.6                           | 76.4                           | 0.589                      | 0.722                          | 0.925             | 1.077             |

*Specific Gravity of Sulphuric Acid at 15° C. (Kolb).—contd.*

| °B. | Specific Gravity. | 100 parts by weight contain |  |                          |                          | 1 litre contains kilos. of |                                  |                |                |
|-----|-------------------|-----------------------------|--|--------------------------|--------------------------|----------------------------|----------------------------------|----------------|----------------|
|     |                   | SO <sub>3</sub> per cent.   | H <sub>2</sub> SO <sub>4</sub> per cent. | Acid of 60° B. per cent. | Acid of 53° B. per cent. | SO <sub>3</sub> .          | H <sub>2</sub> SO <sub>4</sub> . | Acid of 60° B. | Acid of 53° B. |
| 43  | 1.424             | 42.9                        | 52.8                                     | 67.4                     | 78.5                     | 0.611                      | 0.749                            | 0.960          | 1.108          |
| 44  | 1.438             | 44.1                        | 54.0                                     | 69.1                     | 80.6                     | 0.634                      | 0.777                            | 0.994          | 1.159          |
| 45  | 1.453             | 45.2                        | 55.4                                     | 70.9                     | 82.7                     | 0.657                      | 0.805                            | 1.030          | 1.202          |
| 46  | 1.468             | 46.4                        | 56.9                                     | 72.9                     | 84.9                     | 0.681                      | 0.835                            | 1.070          | 1.246          |
| 47  | 1.483             | 47.6                        | 58.3                                     | 74.7                     | 87.0                     | 0.706                      | 0.861                            | 1.108          | 1.290          |
| 48  | 1.498             | 48.7                        | 59.6                                     | 76.3                     | 89.0                     | 0.730                      | 0.893                            | 1.143          | 1.330          |
| 49  | 1.514             | 49.8                        | 61.0                                     | 78.1                     | 91.0                     | 0.754                      | 0.923                            | 1.182          | 1.378          |
| 50  | 1.530             | 51.0                        | 62.5                                     | 80.0                     | 93.3                     | 0.780                      | 0.956                            | 1.224          | 1.427          |
| 51  | 1.540             | 52.2                        | 64.0                                     | 82.0                     | 95.5                     | 0.807                      | 0.990                            | 1.268          | 1.477          |
| 52  | 1.563             | 53.5                        | 65.5                                     | 83.9                     | 97.8                     | 0.836                      | 1.021                            | 1.311          | 1.529          |
| 53  | 1.580             | 54.9                        | 67.0                                     | 85.8                     | 100.0                    | 0.867                      | 1.059                            | 1.355          | 1.580          |
| 54  | 1.597             | 56.0                        | 68.6                                     | 87.8                     | 102.1                    | 0.894                      | 1.095                            | 1.402          | 1.636          |
| 55  | 1.615             | 57.1                        | 70.0                                     | 89.6                     | 104.5                    | 0.922                      | 1.131                            | 1.447          | 1.688          |
| 56  | 1.634             | 58.4                        | 71.6                                     | 91.7                     | 106.9                    | 0.954                      | 1.170                            | 1.499          | 1.747          |
| 57  | 1.652             | 59.7                        | 73.2                                     | 93.7                     | 109.2                    | 0.986                      | 1.210                            | 1.548          | 1.804          |
| 58  | 1.672             | 61.0                        | 74.7                                     | 95.7                     | 111.5                    | 1.019                      | 1.248                            | 1.599          | 1.863          |
| 59  | 1.691             | 62.4                        | 76.4                                     | 97.8                     | 114.0                    | 1.055                      | 1.292                            | 1.654          | 1.928          |
| 60  | 1.711             | 63.8                        | 78.1                                     | 100.0                    | 116.6                    | 1.092                      | 1.336                            | 1.711          | 1.995          |
| 61  | 1.732             | 65.2                        | 79.0                                     | 102.3                    | 119.2                    | 1.129                      | 1.384                            | 1.772          | 2.065          |
| 62  | 1.753             | 66.7                        | 81.7                                     | 104.6                    | 121.9                    | 1.169                      | 1.432                            | 1.838          | 2.137          |
| 63  | 1.774             | 68.7                        | 84.1                                     | 107.7                    | 125.5                    | 1.219                      | 1.492                            | 1.911          | 2.226          |
| 64  | 1.796             | 70.6                        | 86.5                                     | 110.8                    | 129.1                    | 1.268                      | 1.554                            | 1.990          | 2.319          |
| 65  | 1.819             | 73.2                        | 89.7                                     | 114.8                    | 138.8                    | 1.332                      | 1.632                            | 2.088          | 2.434          |
| 66  | 1.842             | 81.6                        | 100.0                                    | 128.0                    | 149.3                    | 1.503                      | 1.842                            | 2.358          | 2.750          |

*Specific Gravity of Highly Concentrated Sulphuric Acid (Lange and Nef).*

| H <sub>2</sub> SO <sub>4</sub> per cent. | Specific Gravity. | °B.  | H <sub>2</sub> SO <sub>4</sub> per cent. | Specific Gravity. | °B.  |
|--|-------------------|------|--|-------------------|------|
| 90                                       | 1.8185            | 65.1 | *95.97                                   | 1.8406            | 66.0 |
| *90.20                                   | 1.8195            |      | 97                                       | 1.8406            |      |
| 91                                       | 1.8241            | 65.4 | 97                                       | 1.8410            |      |
| *91.48                                   | 1.8271            |      | *97.70                                   | 1.8413            |      |
| 92                                       | 1.8294            | 65.6 | 98                                       | 1.8412            |      |
| *92.83                                   | 1.8334            |      | *98.39                                   | 1.8406            |      |
| 93                                       | 1.8339            | 65.8 | *98.66                                   | 1.8409            |      |
| 94                                       | 1.8372            | 65.9 | 99                                       | 1.8403            |      |
| *94.84                                   | 1.8387            |      | *99.47                                   | 1.8395            |      |
| 95                                       | 1.8390            | 66.0 | *100.00                                  | 1.8384            |      |

Turkey red oil (sulpholeate); together with sodium sulphate ( $\text{NaHSO}_4$ ) as a substitute for tannin; in the preparation of indigo carmine (fuming sulphuric acid); in mordanting wool with bichromate and sulphuric acid; for cleaning copper pans, etc., etc.

**Fuming or Nordhausen Sulphuric Acid,**  $\text{H}_2\text{SO}_4 +$  (varying quantities of)  $\text{SO}_3$ .

A solution of sulphuric anhydride in sulphuric acid. It is valued according to the proportion of free anhydride, which must be estimated in assessing the value. Sulphurous acid, which may be present, must also be estimated by means of standard iodine solution and deducted from the total acid. All the processes described in the literature for the evaluation of fuming sulphuric acid (Clau and Gaier, *Chem. Ind.*, iv., 251; Lange and Harter, *Alkali Makers' Pocket-book*, 1881, 100; Winkler, etc.), are not sufficiently quick and simple for practical use. The following method is easy and certain of execution, and, whilst requiring little time, gives accurate results. A dry ordinary thin-walled test-tube (about 18 mm. wide) is drawn out, about 4 cms. from the bottom, to a capillary 3 to 4 cms. long. It is weighed, and the capillary dipped into the acid, which is best contained in a narrow-necked flask, and should have been thoroughly mixed. The upper part of the tube is then heated by means of a Bunsen burner until so much air has been expelled that 8 to 10 grammes of the acid enter the tube on cooling. The capillary is at once fused together, the glass cleaned, again weighed and brought into a thick-walled, stoppered litre flask containing 200 to 300 c.c. of water. The test-tube is then broken by shaking the flask, cooling at the same time, the fumes of anhydride are absorbed by the water within a few minutes. When this has occurred and the contents have cooled, they are separated from the broken glass by running through a funnel, made up to 1,000 c.c. and 250 c.c. titrated with normal caustic soda.

Example: 9.7104 grammes of fuming sulphuric acid taken; the 250 c.c. required 52.38 c.c. of normal soda.  $52.38 \times 0.04 \times 4 = 8.3808$  grammes of  $\text{SO}_3$  in 9.7104

grammes of acid = 86.3 per cent. of  $\text{SO}_3$ ;  $100 - 86.3 = 13.7$  per cent. of water, which is united to  $\text{SO}_3$ ; 13.7 of water correspond to  $13.7 \times 4.44 = 60.82$  per cent. of  $\text{SO}_3$  combined with the water. Thus  $86.3 - 60.82 = 25.48$  per cent. of  $\text{SO}_3$  is present in the anhydrous condition. If, further, we were to find, by titration of the sulphurous acid with iodine solution, 0.16 per cent. of  $\text{SO}_2$ , then, since 0.16 gramme of  $\text{SO}_2 = 0.20$  gramme of  $\text{SO}_3$ , there would be present  $25.48 - 0.20 = 25.28$  per cent. of  $\text{SO}_3$  as pure anhydride.

*Application.* To dissolve indigo in preparing indigo carmine; in making Turkey red oils and olive oil emulsions for Turkey red dyeing.

#### SULPHATES.

Sulphates are frequently adulterated, or contaminated, by chlorides, sand, free acids, carbonates, iron and other metals. As in the case of the chlorides, the general requirements are dryness, complete solubility and neutrality. The more important sulphates are mentioned individually.

**Sodium Sulphate, Glauber's Salt,**  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} = 322$ ; solubility, cold water = 5:100, hot water = 42.5:100.

Sodium chloride is a frequent impurity.

*Application.*—In wool-dyeing, generally together with sulphuric acid, or as the technical bisulphate ("Tartar substitute"). It causes the fibre to take up the dye more evenly.

**Sodium Bisulphate, Tartar Substitute,**  $\text{NaHSO}_4 \cdot \text{H}_2\text{O} = 138$ ; very soluble in water.

The acidity may be estimated by titration with normal caustic soda, 1 c.c. = 0.138 gramme of  $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ .

*Application.*—As sodium sulphate, generally only in wool-dyeing, more rarely in silk-dyeing.

**Calcium Sulphate, Gypsum,**  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} = 172$ ; solubility, cold water = 1:490; hot water = 1:460.

Frequently contains carbonate, alkaline sulphate and chloride.

*Application.*—In dressing and weighting fabrics.

**Magnesium Sulphate, Epsom Salts,**  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  = mol. wt. 246.3; solubility, cold water  $\approx 26$ , 100°, hot water = 71.5 : 100.

Often contains chlorides and foreign (alkali) metals.

*Application.* Almost exclusively in finishing; without injury a quantity 4 to 6 times greater than the permissible amount of magnesium chloride may be added. It makes the fabric thicker, moister and softer.

This salt is also added, as an adulterant, to tin crystals and tannin (which see).

**Lead Sulphate,**  $\text{PbSO}_4$  = mol. wt. 303.2, solubility, cold water = 1 : 22,800, hot water very slight.

Comes into commerce in paste form, and is often adulterated by barium sulphate and gypsum.

*Application.* In printing blues.

**Ferrous Sulphate, Green Vitriol, Copperas,**  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  = mol. wt. 277.84, solubility, cold water = 60 : 100; hot water = 333 : 100; 25.85 per cent. of  $\text{FeO}$ .

Commercial ferrous sulphate is generally fairly pure. As impurities it contains more or less ferric oxide, lime, chlorine, free sulphuric acid, occasionally also copper, zinc and alum. Copper is especially harmful to the alizarine dyes; zinc and alumina are also to be avoided. According to the intended use, a greater or less degree of oxidation is permissible and desired. Alumina is detected by precipitating the iron from a boiling solution with caustic soda, after previous oxidation with nitric acid or bromine water. The alumina remains dissolved and is precipitated as hydrate from the filtrate on adding excess of ammonium chloride (or hydrochloric acid so acid reaction and then ammonia to alkaline reaction).

The value is essentially determined by the proportion of total and ferrous iron.

*Total iron* is estimated gravimetrically by precipitating the oxidised solution with ammonia, filtering and igniting to  $\text{Fe}_2\text{O}_3$ , or volumetrically as described in detail under *Ferric Sulphate* (which see).

*Ferrous Oxide.*—(a) The ferrous oxide is estimated by direct titration with permanganate: 50 grammes are dissolved to 1,000 c.c.; to 50 c.c. of the solution are added



20 c.c. of sulphuric acid (1 : 3) and the mixture then titrated with  $\frac{1}{10}$  N permanganate, 1 c.c. of which = 0.01437 gramme of FeO = 0.05557 gramme of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ .

(b) Bichromate solution may be used instead of permanganate, the process is then the reverse of the titration of chromic acid by ferrous salt (see *Potassium Bichromate*), 1 c.c. of  $\frac{1}{10}$  N potassium bichromate = 0.007184 gramme of FeO or 0.02778 gramme of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ .

The difference between the total iron and ferrous iron corresponds to the ferric oxide, 1 c.c. of  $\frac{1}{10}$  N permanganate = 0.01597 gramme of  $\text{Fe}_2\text{O}_3$ .

*Applications.*—Very extensive. In indigo-dyeing (1 part of indigo, 3.5 to 4 parts of ferrous sulphate, 4 parts of lime); in dyeing cotton black, in alizarine-dyeing, in dyeing wool black, for iron chamois. Ferrous sulphate often comes into the market mixed with copper sulphate.

**Aluminium Sulphate, Sulphate of Alumina,**  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  = 664.8; solubility, cold water = 85 : 100; hot water = 1,130 : 100.

As impurities are found: iron, zinc, copper, lead, chromium, alkalis, chlorine, free sulphuric acid.

*Alumina* may be estimated by dissolving 25 grammes to 1,000 c.c., and heating 50 c.c. of the solution with ammonia and ammonium chloride at a temperature near the boiling point, until the ammonia is nearly all driven off. The solution must, however, remain distinctly alkaline. The precipitate is filtered off, dried, ignited, weighed and calculated as  $\text{Al}_2\text{O}_3$ .

In the precipitate iron may be estimated colorimetrically and deducted from the alumina.

The *basicity* may be estimated as in ferric sulphate (which see).

*Free sulphuric acid* is detected by tropaeolin OO. Watson Smith (*Journ. Soc. Dyers and Col.*, 1884, 35) recommends for this purpose ferric acetate, which loses its red colour in the presence of traces of mineral acids. The free acid can be approximately estimated by titration of an alcoholic extract of the sulphate with  $\frac{1}{10}$  N alkali and phenolphthalein.

The most accurate method is that of Beilstein and Grosset

(*Zeits. anal. Chem.*, 1890, 77): 1 to 2 grammes of the sulphate are dissolved in 5 c.c. of water, 15 c.c. of a cold saturated neutral solution of ammonium sulphate added, and the mixture stirred for fifteen minutes; 50 c.c. of 95 per cent. alcohol are then added, when the whole of the aluminium sulphate is precipitated as ammonia alum, whilst the free sulphuric acid remains in solution. The liquid is filtered, the whole or an aliquot part evaporated on the water-bath, the residue taken up in water and titrated with  $\frac{1}{10}$  N caustic soda and phenolphthalein.

Iron can be detected and estimated colorimetrically with potassium ferro- or ferricyanide, tannin, potassium sulphocyanide, etc. H. v. Kéler has carried out an exhaustive research on the permissible amount of iron in aluminium sulphate. The results were as follows: aluminium sulphate for Turkey red dyeing should not contain more than 0.001 per cent. of total iron, a larger quantity is harmful; ferric salts are more harmful than ferrous. In calico-printing the iron may rise to 0.00524 per cent., more may be harmful. Zinc salts are always harmful.

*Application.*—Very extensive as a mordant in dyeing and printing, as a waterproofing material, etc. For cotton generally used as basic salt (1 kilo. of normal salt + 160 grammes of calcined soda), followed by fixing with ammonia, ammonium carbonate, sodium phosphate, arsenate or silicate, soap, Turkey red oil for wool, cold to hot, as normal salt with tartar (4:3); for silk the normal and basic salt, the fabric remains in the cold solution twelve to twenty-four hours (also see *Alum*).

**Ferric Sulphate, Nitrate of Iron, Iron Mordant,  $\text{Fe}_2(\text{OH})_2(\text{SO}_4)_2$  to  $\text{Fe}_4(\text{OH})_2(\text{SO}_4)_6$ .**

Ferric sulphate is the best for most purposes when its composition corresponds to the formula  $\text{Fe}_3(\text{OH})_6(\text{SO}_4)_4$ , i.e., when  $\text{SO}_3 : \text{Fe}_2\text{O}_3 = 1 : 1.125$ . As a rule it is more acid. It is advisable to take care that the basicity is always, as far as possible, the same, since the basicity is of the greatest importance to the mordant.

The following are characteristics of commercial preparations:—

| No. | $\text{Fe}_2\text{O}_3$<br>per cent. | $\text{SO}_3$<br>per cent. | $\text{FeO}$<br>per cent. | Cl.<br>$\text{N}_2\text{O}_5$ . | Ratio<br>$\text{SO}_3 : \text{Fe}_2\text{O}_3$ . |
|-----|--------------------------------------|----------------------------|---------------------------|---------------------------------|--|
| I   | 18.4                                 | 22.0                       | 0.1                       | trace                           | 1 : 1.2  |
| II  | 19.4                                 | 23.3                       | 0.25                      | —                               | 1 : 1.2  |
| III | 21.7                                 | 25.0                       | 0.30                      | —                               | 1 : 1.15   |
| IV  | 21.16                                | 24.23                      | 0.35                      | —                               | 1 : 1.14   |

If the mordant is too basic, the fabric is injured and the mordant readily separates precipitates: if it is too acid, too little ferric oxide is fixed. However, the requirements of consumers vary from time to time.

A complete examination would be similar to that of stannic chloride; the following would be determined. specific gravity (picnometer, hydrometer), ferrous oxide, total iron, ferric oxide, total acid, sulphuric acid, chlorine, nitric acid, alkalis, etc.

The *specific gravity* is taken by means of a 50 c.c. specific gravity bottle; this 50 c.c. is then diluted to 1,000 c.c.

*Ferrous Oxide.*—200 c.c. of this solution are acidified with sulphuric acid and titrated with  $\frac{1}{10}$  N permanganate, 1 c.c. of which = 0.01117 gramme of  $\text{FeO}$  = 0.01117 gramme of  $\text{Fe}$ .

*Total Iron and thence Ferric Oxide.* (a) 20 c.c. of the dilute solution are reduced with about 20 grammes of zinc (granulated or in rods) and an excess of sulphuric acid, until the solution no longer gives a reaction with potassium sulphocyanide. The reduction is performed in a small flask with a Bunsen valve. The solution is then poured off from the undissolved zinc, sulphuric acid added, and titrated with  $\frac{1}{10}$  N permanganate. The undissolved zinc is weighed and allowance made for the consumption of permanganate by the dissolved zinc (this correction is determined once for all for the particular sample of zinc, by titrating a solution of 50 to 100 grammes in sulphuric acid). The difference between total iron and ferrous iron gives the ferric oxide, e.g., 7 grammes of zinc, when dissolved in sulphuric acid, require 0.1 c.c. of  $\frac{1}{10}$  N permanganate; 14 grammes of zinc were used (= 0.2 c.c. of permanganate), and in the titration 20.55 c.c. of permanganate were required, or deducting the

0.2 c.c. due to the zinc, 20.35 c.c. Therefore in 1 c.c. of the solution there is  $20.35 \times 0.01597 = 0.3250$  gramme of  $\text{Fe}_2\text{O}_3$ . The specific gravity of the solution was found to be 1.53834, thence  $1.53834 : 0.3250 = 100 : x$ , or  $x = 21.13$  per cent. of  $\text{Fe}_2\text{O}_3$ . If the ferrous oxide previously found be deducted, the result gives the iron present as ferric oxide.

(b) The total iron may also be estimated gravimetrically by precipitating 20 c.c. of the solution with ammonia. It is then heated near the boiling point until the smell of ammonia becomes slight, the precipitate filtered off, ignited and weighed as  $\text{Fe}_2\text{O}_3$ . If ferrous salt be present, which is generally the case, before precipitation the solution is oxidised with 2 to 3 drops of dilute nitric acid.

*Total Acid.*—(a) 100 c.c. of the solution are mixed in a 500 c.c. flask with 60 or 70 c.c. of normal soda, the mixture boiled, allowed to cool, made up to 500 c.c. and an aliquot part (250 c.c.) filtered. The excess of soda is now estimated by titration with normal sulphuric acid and methyl orange. From the excess the amount used is calculated; 1 c.c. of normal soda = 0.040 gramme of  $\text{SO}_3$ .

Example: 100 c.c. of solution + 60 c.c. of normal soda made up to 500 c.c.; 200 c.c. require 4.525 c.c. of normal sulphuric acid;  $200 : 4.525 = 500 : x$ ;  $x = 11.31$ ,  $60 - 11.31 = 48.69$  c.c. of normal soda used;  $48.69 \times 0.04 = 1.9476$  grammes of  $\text{SO}_3$ ; 100 c.c. of solution correspond to 7.7906 grammes of mordant.  $7.7906 : 1.9476 = 100 : x$ , thence  $x = 25.00$  per cent. of  $\text{SO}_3$ .

(b) The following process for the estimation of the total acid is simpler. 50 c.c. of the solution are decomposed with much hot water, heated for some time until the decomposition is complete (on the water-bath or over the naked lamp to near the boiling-point), and this solution, without filtering, titrated directly with normal soda, using phenolphthalein as indicator. Direct titration is permissible here, which is not the case with the chlorides of tin, because excess of soda has no action upon the ferric hydroxide. The method is accurate. In approaching the end of the titration, the liquid is allowed to stand for a moment from time to time, in order that it may be seen, from the supernatant solution, whether the

acid is neutralised or not, *i.e.*, whether the liquid is rose-coloured or still colourless. 1 c.c. of normal soda = 0.04 gramme of  $\text{SO}_3$ .

*Sulphuric Acid.*—If it is required to estimate the sulphuric acid as such, and not merely the total acid, it is precipitated in 10 c.c. of the solution by barium chloride, and the barium sulphate weighed in the ordinary manner. The weight of barium sulphate multiplied by 0.343 gives the  $\text{SO}_3$ . The difference between the total acid and sulphuric acid is to be ascribed to foreign acids—hydrochloric, nitric, sulphurous. The smaller the quantity of these foreign acids, the better. In the case of a good mordant the difference should not materially exceed 1 per cent.

*Hydrochloric acid* may also be estimated in the ordinary manner by means of silver, but this is seldom required.

*Nitric acid*, which is almost always present in appreciable quantity, may be titrated by means of indigo solution as in water, or estimated by the gasometric method.

*Practical Test.*—In the case of iron mordant a practical test is often very important; it may be carried out with wool or silk. For example, several skeins of cotton each of 10 grammes weight are well washed and stirred in a decoction of tannin, sumach, etc., for one hour, taken out, unwound and immersed in dilute solutions of the sample (5 c.c. in 250 c.c. of water) or of a standard sample of known quality. After twenty to thirty minutes they are taken out, washed, dried and compared. They may also be dyed with logwood. Silk is weighed before and after the experiment, in order to estimate the quantity of ferric oxide fixed. The more iron is fixed on the fibre, the better is the mordant, other things being equal. The weighed silk (the largest convenient amount) is mordanted for one hour in a solution of 30° B., well washed, treated with water at 50° C., then with Marseilles soap at the boil, washed, dried at the ordinary temperature and weighed.

*Application.*—Commercial ferric sulphate is generally a solution of 50° to 60° B.; it is principally used as a solution of 30° B. in black silk-dyeing as weighting and bottoming for Prussian blue; it is used for similar purposes in black

cotton-dyeing, in printing the so-called "dyers' black," which has in recent years been largely supplanted by aniline black.

**Copper Sulphate, Blue Vitriol, Bluestone,**  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$   
= mol. wt. 249.6; solubility, cold water = 40:100; hot water = 203:100; 25.47 per cent. Cu.

The value is according to the percentage of pure copper sulphate; the salt should also give a clear solution in water, and not contain too much iron, lime and alkali salts (or zinc).

25 grammes are dissolved to 1,000 c.c.

*Sulphuric Acid.*—25 c.c. of this solution are acidified with hydrochloric acid and precipitated with barium chloride, the barium sulphate is weighed and calculated to sulphuric acid.

*Copper.*—25 c.c. are acidified with sulphuric acid and precipitated with sulphuretted hydrogen.

(a) The copper sulphide is either ignited in a Rose crucible with fine precipitated sulphur in a current of hydrogen to constant weight; or

(b) the sulphide is roasted, moistened with nitric acid and ignited to constant weight, by which process it is quantitatively converted into copper oxide,  $\text{CuO}$ , or

(c) 25 c.c. of the solution are precipitated with caustic soda, the liquid boiled for some time, filtered after well washing by decantation, the precipitate well washed on the filter until the filtrate is neutral, then dried, ignited and weighed as  $\text{CuO}$ ;  $79.57 \text{ CuO} = 79.57 \text{ Cu}_2\text{S} = 63.57 \text{ Cu} = 249.63 \text{ CuSO}_4 \cdot 5\text{H}_2\text{O}$ , or

(d) the copper is estimated by one of the many volumetric processes (see Fresenius, *Quant. Anal.*, I. 258). The Volhard-Henriques method, though little used, must be regarded as the best, since it is rapid and easy of execution, very accurate and requires no special solutions. 30 grammes of copper sulphate are dissolved to 500 c.c., 5 c.c. of the solution are mixed with excess of sulphurous acid in a 100 c.c. flask and 20 c.c. of  $\frac{1}{10}$  N ammonium sulphocyanide added, the flask is filled up to the mark, well shaken and the liquid filtered; 50 c.c. of the filtrate are mixed with 10 c.c. (excess) of  $\frac{1}{10}$  N silver nitrate solution,

acidified with nitric acid, iron alum added as indicator, and the excess of silver titrated with  $\frac{1}{10}$  N ammonium sulphocyanide, until the red coloration appears.

Calculation: Suppose that 5.6 c.c. of  $\frac{1}{10}$  N sulphocyanide solution are used in titrating the excess of silver, then in 2.5 c.c. of the original solution there is  $5.6 \times 0.003178$  gramme of Cu =  $5.6 \times 0.012478$  gramme of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , from which the percentage may be calculated.

*Iron.* 200 c.c. of the solution are oxidised with two drops of nitric acid and precipitated by excess of ammonia. The copper goes into solution, the iron is precipitated, it is filtered off, or redissolved and again precipitated, ignited and weighed as  $\text{Fe}_2\text{O}_3$ , or estimated colorimetrically.

*Application.*—Used as an oxidising agent for aniline black (copper sulphide is also used, it is prepared from the sulphate); in dyeing browns with catechu (25 parts of copper sulphate to 100 parts of catechu); in dyeing a blue from acid green + acid violet ( $\frac{1}{2}$   $\text{CuSO}_4$  +  $\frac{2}{3}$  alum); for “Jäger” green; in mordanting wool for logwood blacks; for an after-treatment of many direct-dyeing colouring matters, such as benzoazurine, in order to increase the fastness to light, for “chrome” black (0.5 per cent.  $\text{K}_2\text{Cr}_2\text{O}_7$  + 1 per cent.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , or 2 per cent.  $\text{K}_2\text{Cr}_2\text{O}_7$  + 1.5 per cent.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), etc.

#### ALUMS.

Potash alum,  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  = mol. wt. 948.4; solubility, cold water = 9.5:100; hot water = 35.7:100.

Soda alum,  $\text{Na}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  = mol. wt. 916.2; solubility, cold water = 110:100; hot water, very soluble.

Ammonia alum,  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  = mol. wt. 906.2; solubility, cold water = 9:100; hot water = 42.2:100.

Iron alum,  $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$  = mol. wt. 1005.9; solubility, cold water = 20:100; hot water, very soluble.

Chrome alum,  $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$  = mol. wt. 998.2; solubility, cold water = 20:100; hot water = 50:100; 13.5 per cent. of  $\text{Cr}_2\text{O}_3$ .

The alums are extensively used in the textile industries.

The commercial article is generally very pure. In an examination the following points are to be considered: In the case of potash and soda alums the percentage of alumina is of the first importance; the percentage of water may also be taken, and free acid (as with aluminium sulphate) and iron tested for. The same may be said of ammonia alum. In the case of iron alum iron, in chrome alum chromium occupies the place of aluminium; the proportion of these two metals indicates the purity of the compound. Iron alum should also contain no ferrous sulphate, or very little (detected and estimated as in ferrie sulphate). Chrome alum, which is generally used in the state of the basic sulphate  $\text{Cr}_2(\text{SO}_4)_3(\text{OH})_2$ , frequently contains tarry matter, gypsum and sodium sulphate, all of which should, as far as possible, be absent. The chromium is estimated by precipitation with ammonia. If the chrome alum gives an intense iron reaction, the chromium must be separated from the iron. In other respects a detailed examination is to be conducted as with the corresponding sulphates.

*Application.*—Very extensive. In dyeing with certain dyestuffs such as Victoria blue (3 to 5 per cent. of alum + acetic acid), etc.; as a mordant in alizarine-dyeing; in wool-dyeing as a mordant (7 to 10 per cent. of alum + 1 per cent. of tin crystals), almost entirely replaced by potassium bichromate; in cochineal-dyeing (10 to 12 per cent. of alum + 2 to 3 per cent. of tartar); in dyeing flannel with ponceaux, replacing cochineal (0.5 to 1 per cent. of alum + ponceau + trace of stannic chloride); in dyeing cosine on wool (alum gives a very bright cosine lake); with water blue, or Turkey red dyeing (for this purpose alum must be free from iron or at most contain 0.001 per cent.; solutions of 1 B to 5 to 8 B are used as mordants); with indom blue; in printing on wool (alizarine orange and red).

Iron alum is little used: as a mordant for wool blacks, occasionally also for alizarine.

Chrome alum is also rarely used. It is principally important as forming the starting point for the preparation of other chromium salts, *e.g.*, chromium acetate, chloride, etc. It has also been recommended for mordanting wool, but it



has not been introduced, since it does not precipitate the chromium oxide quite evenly on the fibre, and cannot in this property equal potassium bichromate.

#### NITRIC ACID AND NITRATES.

**Nitric Acid.**— $\text{HNO}_3$  = mol. wt. 63. When no foreign acid is present, the strength may be estimated by means of the specific gravity, or volumetrically. 50 grammes are diluted to 1,000 c.c. and 50 c.c. of the solution titrated with normal caustic soda, 1 c.c. of which = 0.063 gramme of  $\text{HNO}_3$ .

In testing for impurities, chlorine, sulphuric acid, metals, iron, alkali salts and nitrous acid may be expected. If the acid is contaminated by other acids and the proportion of pure nitric acid is to be determined, the nitric oxides may be estimated. However, nitric acid is of so little importance in the textile industries that it is not necessary to introduce this complicated gasometric method here.

*Application.*—Very restricted. In colouring nitrogenous materials (feathers, silk) which become yellow by reason of the nitro-compounds produced, but are at the same time considerably weakened (2 parts of  $\text{HNO}_3$  + 1 part  $\text{HCl}$  diluted to 2° B.); in the production of imitation selvages on fabrics for export (nitric acid + gum + starch printed on, in order to give the appearance of yarn-dyed fabrics, which have yellow selvages); as a reagent for indigo, which does not now give a distinguishing reaction, since many other blues give the same spot, *e.g.*, the blue obtained from acid green + acid violet; for engraving printing rollers.

**Sodium Nitrate, Chili Saltpetre,** mol. wt.  $\text{NaNO}_3$  = 85; solubility, cold water = 80 : 100; hot water = 200 : 100.

Nitric acid is estimated, as in water, by means of indigo solution. Chloride and sulphate occur as impurities.

*Application.*—Very restricted. occasionally used for the after-oxidation of aniline black.

**Silver Nitrate.**— $\text{AgNO}_3$  = mol. wt. 169.9; solubility, cold water = 120 : 100; hot water = 1,000 : 100.

The percentage of silver is all-important. The salt is

titrated with decinormal sodium chloride solution, using neutral potassium chromate as indicator, until the brown coloration just appears; 1 c.c. of decinormal NaCl solution = 0.017 gramme of  $\text{AgNO}_3$ .

*Application.*—Almost only for marking inks ( $\text{AgNO}_3 + \text{NH}_3 + \text{gum}$ , written or stamped on). The writing is not as sensitive to dilute alkalis and acids as to chlorine.

**Lead Nitrate**,  $\text{Pb}(\text{NO}_3)_2$  = mol. wt. 331.2; solubility, cold water = 48.3 : 100, hot water = 139 : 100.

The percentage of lead indicates the value, it is precipitated as sulphate by means of sulphuric acid, filtered, ignited and weighed as  $\text{PbSO}_4$ .

• *Application.*—For chrome yellow and orange; as the starting point for other lead compounds.

**Ferrous Nitrate**,  $\text{Fe}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  = mol. wt. 287.9; soluble in cold water, decomposed by hot water.

Examined in a similar manner to ferrous sulphate. Nitric acid estimated as in sodium nitrate.

*Application.* Now rarely or never used; for rust yellow on cotton, Prussian blue on wool.

**Ferric Nitrate**,  $\text{Fe}_2(\text{NO}_3)_6 \cdot 18\text{H}_2\text{O}$  = mol. wt. 807.7; readily soluble in hot and cold water.

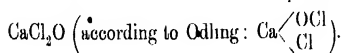
Examined as ferric sulphate, except in regard to the nitric acid. To be tested for sulphuric acid.

*Application.*—As restricted as the last-mentioned compound; in black cotton-dyeing; in silk-dyeing it has been entirely replaced by basic ferric sulphate.

**Rarer Nitrates.**—For certain special purposes in printing the following nitrates are occasionally used; they are obtained by double decompositions: calcium, aluminum, magnesium, copper and chromium nitrates, the double chromium nitrate acetate.

### CHLORINE-OXYGEN COMPOUNDS.

**Bleaching Powder** is a mixture, in varying proportions, of calcium hypochlorite, chloride and hydroxide with water. The active constituent is best expressed by the formula



The value is always determined by the "available chlorine". According to Schutzenberger, however, the compound does not act by means of the chlorine, but by reason of the free oxygen produced by its decomposition ( $\text{CaCl}_2\text{O} = \text{CaCl}_2 + \text{O}$ ). There are the following methods for the estimation of the chlorine.

I. Gay Lussac's method. The bleaching powder is titrated in aqueous solution with sodium arsenite, using indigo as the indicator. This method has long been disused on account of its inaccuracy in dilute solution arsenious acid no longer has any action.

II. Pennot's method with alkaline arsenic solution and potassium iodide starch paper as indicator.

III. Iodometric methods.

The two latter are most generally used, they will be briefly described.

II. (a) Pennot's solution: 4.438 grammes of pure arsenious acid and 13.0 grammes of pure crystallised soda are dissolved in 600 to 700 c.c. of warm water and the solution made up to 1,000 c.c. when cold; 1 c.c. of the solution corresponds to 0.004438 gramme of  $\text{As}_2\text{O}_3$  or 1 c.c. of chlorine gas at 0° C. and 760 mm. pressure.

10 grammes of bleaching powder are well ground with water and the paste, together with the residue, filled up to 1,000 c.c.; 50 c.c. of the solution are titrated with the above Pennot's solution, until no blue coloration is produced on potassium iodide starch paper, which is the case when all the active chlorine has been used.

Example. 50 c.c. of bleaching powder solution required 40 c.c. of Pennot's solution, i.e., 50 c.c. of bleaching powder solution correspond to 40 c.c. of chlorine gas, or 0.5 gramme of bleaching powder gives off 40 c.c. of chlorine, hence 1 kilo. of bleaching powder can evolve 80 litres of chlorine measured as 0° C. and 760 mm. pressure ( $2\text{CaCl}_2\text{O} + \text{As}_2\text{O}_3 = 2\text{CaCl}_2 + \text{As}_2\text{O}_5$ ).

(b) In place of Pennot's solution,  $\frac{1}{10}$  N arsenic solution (4.948 grammes of pure  $\text{As}_2\text{O}_3$  dissolved by means of soda to 1,000 c.c.) may be used; 1 c.c. of  $\frac{1}{10}$  N sodium arsenite solution = 0.003546 gramme of available chlorine.

III. Iodometric methods: 7.1 grammes of bleaching powder are ground with water and the mixture made up to 1,000 c.c.; 50 c.c. (= 0.3546 gramme) are measured by means of a pipette into a beaker containing 1 litre of distilled water, 1 gramme of potassium iodide and about 10 drops of hydrochloric acid are then added. The liquid is stirred round slowly once, and  $\frac{1}{10}$  N thiosulphate run in quickly from a burette, without stirring, until the colour is slightly yellow. Starch solution is then added and the titration continued slowly until the blue colour disappears.  $\text{Cl}_2 + 2\text{KI} = 2\text{KCl} + \text{I}_2$ ;  $\text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 = \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$ ; 1 c.c. of  $\frac{1}{10}$  N thiosulphate = 0.003546 gramme of chlorine. If, for example, 35.25 c.c. of  $\frac{1}{10}$  N thiosulphate are used, then the percentage of available

$$\text{chlorine} = \frac{35.25 \times 0.003546 \times 100}{0.3546} = 35.25, \text{ i.e., 1 c.c. of}$$

$\frac{1}{10}$  N thiosulphate = 1 per cent. of available chlorine.

IV. The method of Baumann (*Zeits. angew. Chem.*, 1890, 73) may also be mentioned, it is based upon adding hydrogen peroxide and titrating with potassium permanganate.  $\text{CaCl}_2\text{O} + \text{H}_2\text{O}_2 = \text{CaCl}_2 + \text{H}_2\text{O} + \text{O}_2$ . The excess of hydrogen peroxide is titrated with permanganate:  $2\text{KMnO}_4 + 5\text{H}_2\text{O}_2 + 3\text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} + 5\text{O}_2$ .

As has already been seen in II. and III. the strength of bleaching powder may be expressed either in chlorometric degrees (II.), as is customary in France, or in percentages of available chlorine (III.), the usual custom in England and Germany. The chlorometric degrees give the number of litres of (available) chlorine gas (measured at 0° C. and 760 mm. pressure) contained in 1 kilo. of bleaching powder; the English and German degrees are percentages of available chlorine. The connection between the two systems is as follows:—

Chlorometric degrees multiplied by 0.3181 = percentage of available chlorine.

Percentage of available chlorine divided by 0.3181 = chlorometric degrees.

| French Scale. | English and German Scale. | French Scale.                 | English and German Scale. |
|---------------|---------------------------|-------------------------------|---------------------------|
| 63            | 20.04                     | 100                           | 31.81                     |
| 70            | 22.27                     | 105                           | 33.40                     |
| 75            | 23.85                     | 110                           | 34.99                     |
| 80            | 25.48                     | 115                           | 36.58                     |
| 85            | 27.04                     | 120                           | 38.17                     |
| 90            | 28.63                     | 125                           | 40.76                     |
|               |                           | (The best bleaching powder.). |                           |

The question whether the deposit or insoluble residue should be included in titrations of bleaching powder is an important point upon which there should be an understanding. Fresenius titrates it together with the solution, other authorities on textile matters take the opposite course, since, as they very properly say, the insoluble matter is unutilised and unutilisable in practice, and in a technical analysis the technical conditions must be considered.

Chemically pure calcium hydrochlorite contains theoretically 48.9 per cent. of chlorine; in the manufacture of bleaching powder, however, a product containing more than 39 per cent. is not obtained.

*Application.*—Bleaching powder is the bleaching material *par excellence* for vegetable materials; at the present time solutions over 1° B. are rarely, if ever, used, whilst formerly they were used at 3° B. and over. At times a few drops of hydrochloric acid are added; acetic and formic acids have also been proposed, but the carbonic acid of the air is quite sufficient. A strong solution is used to produce cream-coloured linen. Wool and silk are turned yellow by chlorine, and are rotted and altered in structure. Cotton is only altered in strong solutions, oxycellulose being formed and the fibre to a certain extent "animalised". In recent years wool has also been treated with chlorine in order to produce certain lustrous and contracted effects.

**Alkaline Hypochlorites.**—Eau de Javelle,  $\text{KOC}$ ; Eau de Labarraque,  $\text{NaOCl}$ .

These compounds are only stable in solution, in the solid state they decompose very rapidly, thus, on evaporation of

the solutions, they produce alkaline chloride and chlorate. They may be evaluated exactly in the same manner, as bleaching powder, since, in this case too, the available chlorine is the valuable constituent.

R. Bauer has proposed the following method for the practical control of the operation of bleaching (*Dingler's Polyt. Journ.*, 1884, 251, 276): A "chlorine tube," 1.5 cm. wide and 50 cms. long and a burette divided into 0.2 c.c. are used. The reagents are hydrochloric acid, solutions of potassium iodide and sodium thiosulphate; 1 c.c. of the latter = 0.001 gramme of chlorine. 10 c.c. of the bleaching liquor are placed in the "chlorine tube," a few c.c. of potassium iodide solution added until, on shaking, no further brown coloration or turbidity occurs; then a few c.c. of hydrochloric acid are added until the turbid solution becomes clear. The thiosulphate solution is now added from the burette, at first rapidly, then in drops, until on gentle shaking the colour becomes paler and finally quite disappears. Each c.c. of thiosulphate solution corresponds to 1 milligramme of chlorine in 10 c.c. of the liquor.

*Application.*—In bleaching for many purposes these solutions are said to be more suitable than bleaching powder. They may not be heated. They are more readily washed out and the material may afterwards be given a sulphuric acid bath. They are said also to have a more energetic action than bleaching powder; dilute solutions only should be used. On account of the higher price as compared with bleaching powder they are, however, little used. Alkaline hypochlorites are also added to certain bleaching mixtures, e.g., "chlorozone".

**Other Hypochlorites:** of aluminium, magnesium, zinc and barium.

The principle of the examination is the same: the active chlorine is estimated. In addition the metal may be determined, since bleaching powder or a cheaper alkaline hypochlorite might be present in large quantity.

*Application.*—In bleaching special materials. Aluminium hypochlorite, also known as "Wilson's bleaching fluid," for particularly delicate materials; magnesium hypochlorite,

"Ramsay's" or "Grouvelle's bleaching fluid," for linen bleaching; zinc hypochlorite is known as "Varrentrapp's bleaching salt". Generally speaking, little used.

**Potassium Chlorate**,  $\text{KClO}_3 = 122.5$ ; solubility, cold water = 7 : 100; hot water = 50 : 100.

The potassium salt is the most important chlorate; it has been largely used since the introduction of aniline black dyeing. The ordinary impurities are metals, earths, chloride, sulphate, nitrate and free chlorine.

A quantitative estimation of the chlorate is generally unnecessary, since the salt is produced in a state of excellent purity. If it is required, the following is the best process: the chlorate is distilled with excess of hydrochloric acid, the chlorine produced led into potassium iodide solution and the liberated iodine titrated with  $\frac{1}{10}$  N thiosulphate, 1 c.c. of which 0.0020427 gramme of  $\text{KClO}_3$ . If, for example, 0.1 gramme of chlorate be taken for the distillation, then, it is 100 per cent. pure, 48.9 c.c. of  $\frac{1}{10}$  N thiosulphate will be required; under these conditions 1 c.c. of  $\frac{1}{10}$  N thiosulphate corresponds to 2.045 per cent. of  $\text{KClO}_3$ .

*Application.* Almost exclusively as an oxidising agent for aniline black, in producing which it acts as an oxygen carrier in a similar manner to copper sulphide, ammonium vanadate, potassium ferrocyanide, manganates, etc. It has the disadvantage of a low solubility in cold water (7 : 100), on which account it may readily crystallise from strong solutions and cause mishaps in the process (streaks on printed calico). In using concentrated solutions and in printing colours, the employment of sodium chlorate, which is considerably more soluble, prevents these separations. Potassium chlorate is also added to certain bleaching mixtures ("chlorozone"). In the preparation of mordants.

**Sodium Chlorate**,  $\text{NaClO}_3 = 106.5$ ; solubility, cold water = 100 : 100; hot water = 200 : 100.

This salt has the advantages over potassium chlorate of greater solubility and cheapness, however the commercial article is not generally as pure as the potassium salt, and must be carefully examined for impurities. In particular large quantities of chlorides and lime, *i.e.*, calcium chloride,

are found. The percentage of chlorate may be determined as in the potassium salt.

*Application.* Similar to potassium chlorate, when it is required to prepare solutions of greater concentration than 7 : 100, frequently potassium chlorate separates from the printing colour when it is not present even in that theoretical amount.

**Aluminium Chlorate,**  $\text{Al}_2(\text{ClO}_3)_6$  = mol. wt. 555.

Is generally prepared by the consumer by double decomposition of potassium chlorate and aluminium sulphate, the solution is then diluted to 20° B. The two component materials (which see) must be examined.

*Application.* Has a restricted use for aniline black on woven cotton.

**Chromium Chlorate,**  $\text{Cr}(\text{ClO}_3)_3$  = mol. wt. 302.1

Is made in a similar manner by the consumer by double decomposition: potassium chromate + potassium chlorate or chrome alum + potassium chlorate. The basic salt is obtained from 975 grammes of neutral chromium chlorate + 75 grammes of freshly precipitated chromium hydroxide. In an examination the proportions of chromium and chloric acid may be estimated.

*Application.* Very restricted. In printing, for fixing wood colours (steam black, steam brown).

**Aniline Chlorate,** see under *Aniline Salts*.

#### SULPHITE COMPOUNDS.

**Sulphurous Acid, Sulphites, Sodium Bisulphite,**  $\text{SO}_2$  = 64.  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$  = 252; solubility, cold water = 25 : 100; hot water = 1 : 1.

These substances are evaluated by the percentage of sulphurous acid, which may be estimated in the aqueous solution of the acid by means of the hydrometer or better—as also in the salts—by volumetric methods.

1. If no other acids are present, titrate with normal caustic soda and a suitable indicator (see Indicators, p. 1 and Table I., also Mohr's *Titrimethoden*, 6 Aufl., 165, *Anal. Polytechn. Journ.*, 250, 530; Ch. Blarez, *Comptes rend.*, 103, 69). Free



sulphurous acid and bisulphites are titrated with normal caustic soda and phenolphthaleïn, the normal sulphites with normal acid and methyl orange. If methyl orange be added to a bisulphite solution, a red coloration indicates an excess of  $\text{SO}_2$  over the quantity required to form  $\text{NaHSO}_3$ , which excess may be estimated by titrating with normal soda to the point of neutrality. If, however, the solution is coloured yellow by methyl orange, normal sulphite is present, which may be estimated by titration with normal acid.

II. The most reliable method is Bunsen's iodometric process, when simply the proportion of sulphurous acid is required, without regard to its state of combination or freedom: 5 grammes of the salt (or a corresponding quantity of aqueous sulphurous acid) are dissolved in 1 litre of water, which has been boiled and allowed to cool in a closed vessel. A portion of the solution is measured with a pipette, diluted with boiled water to such an extent—about 1 : 10— that 100 c.c. contain at most 0.05 gramme of  $\text{SO}_2$ , slightly acidified with sulphuric or hydrochloric acid, a measured excess of  $\frac{1}{10}$  N iodine solution added and the excess titrated by  $\frac{1}{10}$  N thiosulphate, with starch solution as indicator. 1 c.c. of  $\frac{1}{10}$  N iodine solution = 0.0032 gramme of  $\text{SO}_2$ . Not more than 12 c.c. of iodine solution should be used for 100 c.c. of the sulphite solution titrated.

*Application.*—In bleaching and as an “antichlor”; for washing material bleached with permanganate in order to remove the manganese peroxide; as a reducing agent; in printing as a solvent for many dye-stuffs (caeruleum, alizarine blue); many dyes come into the market in the form of double sodium bisulphite compounds. Frequently gaseous sulphur dioxide is used, produced by burning stick sulphur in the sulphur chambers, in which the fabrics to be bleached are hung.

Sodium bisulphite is also known as “leucogen”; more rarely calcium bisulphite is also employed.

The specific gravities of aqueous solutions of sulphur dioxide are given in the following table, together with the strength of the solutions:—

| Specific gravity. | SO <sub>2</sub> per cent. | Specific gravity. | SO <sub>2</sub> per cent. | Specific gravity. | SO <sub>2</sub> per cent. | Specific gravity. | SO <sub>2</sub> per cent. |
|-------------------|---------------------------|-------------------|---------------------------|-------------------|---------------------------|-------------------|---------------------------|
| 1.0028            | 0.5                       | 1.0168            | 3.0                       | 1.0302            | 5.5                       | 1.0126            | 8.0                       |
| 1.0056            | 1.0                       | 1.0194            | 3.5                       | 1.0328            | 6.0                       | 1.0450            | 8.5                       |
| 1.0085            | 1.5                       | 1.0221            | 4.0                       | 1.0353            | 6.5                       | 1.0471            | 9.0                       |
| 1.0113            | 2.0                       | 1.0248            | 4.5                       | 1.0377            | 7.0                       | 1.0497            | 9.5                       |
| 1.0141            | 2.5                       | 1.0275            | 5.0                       | 1.0401            | 7.5                       | 1.0520            | 10.0                      |

**Hydro- or Hypo-sulphurous Acid, Hydro- or Hypo-sulphites,**  $\text{H}_2\text{O} + \text{SO}_2 + \text{Zn} = \text{ZnSO}_3 + \text{H}_2$ ;  $\text{H}_2 + \text{SO}_2 = \text{H}_2\text{SO}_2$ .

Hydrosulphurous acid has recently, in the form of the zinc and calcium salts, attained considerable importance in indigo dyeing (Schutzenberger). It is produced from zinc and bisulphites according to the above equations. The proportion of the bisulphite to the zinc is of certain importance, since the reaction may take place in two ways:  $4\text{NaHSO}_3 + \text{Zn} = \text{ZnSO}_3 + \text{Na}_2\text{SO}_3 + \text{Na}_2\text{S}_2\text{O}_4 + 2\text{H}_2\text{O}$ , and  $3\text{NaHSO}_3 + \text{Zn} = \text{ZnSO}_3 + \text{Na}_2\text{SO}_3 + \text{NaHSO}_2 + \text{H}_2\text{O}$ . When lime is added the zinc is precipitated and calcium hydrosulphite results, which has the property of reducing indigo blue,  $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$ , to indigo white,  $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2$ , containing two hydrogen atoms more. Since these solutions are prepared by the dyer, the quality of the materials and their value must be ascertained.

*Application.*—In the hydrosulphite vat (more suitable for wool): 30 kilos. of bisulphite solution of 32° to 35° B. + 6 to 7 kilos. of zinc dust are stirred with 30 litres of water; the temperature should not be allowed to exceed 35° C. Then 8 litres of caustic soda solution of 38° B. + 7 kilos. of lime, slaked with 30 litres of water, are added. After standing twelve to twenty-four hours, the clear yellow solution, which can reduce about 10 kilos. of indigo, is drawn off.

**Sodium Thiosulphate, "Sodium Hyposulphite."**  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} = 248$ ; solubility, cold water = 102; 100; very soluble in hot water.

The impurities may be carbonate, sulphate, sulphite and free alkali. The percentage of thiosulphate is estimated

volumetrically by iodine solution: 25 grammes are dissolved in 1,000 c.c., and 25 c.c. of the solution titrated by  $\frac{1}{10}$  N iodine solution, with starch solution as indicator. 1 c.c. of iodine solution = 0.024812 gramme of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ .

*Application.*-- In calico-printing to fix metallic oxides; in dyeing as a resist for aniline black; in bleaching to remove the last traces of chlorine from the fibre (hence an "anti-chlor"); in mordanting silk (6 to 8 per cent. of alum + 4 per cent. of thiosulphate); in dyeing wool with eosine; in washing clothes; for precipitating finely divided sulphur upon wool for methyl and malachite greens (Lauth). Also known under the names of "antichlor" and "hyposulphite of soda," or "hypo".

#### MISCELLANEOUS COMPOUNDS.

**Sodium Nitrite**,  $\text{NaNO}_2$  = 69, very soluble in cold and hot water.

This salt has not long been used in the textile industries; its value is estimated by the percentage of nitrite. Heavy metals are frequently found as impurities. The nitrous acid is estimated by oxidation with permanganate, which may be standardised against ferrous ammonium sulphate or silver nitrite, the former compound (also known as Mohr's salt) contains exactly one-seventh of its weight of iron, *i.e.*, 7 grammes of Mohr's salt contain exactly 1 gramme of metallic iron. Good commercial sodium nitrite should contain 95 to 97 per cent. of  $\text{NaNO}_2$ .

About 25 grammes of sodium nitrite are dissolved in 1,000 c.c.; 40 or 45 c.c. of  $\frac{1}{10}$  N permanganate solution are added to 200 c.c. of sulphuric acid (1.5) and the above nitrite solution somewhat rapidly added at 40° C. until decolorisation occurs; then the mixture is titrated back with permanganate until the red coloration remains for five minutes. Lunge's method, according to which the nitrite solution is titrated with permanganate, is unreliable, since in that case some nitrous acid is always lost.  $2\text{Fe} = \text{NaNO}_2$  (111.68 = 69.01).

<sup>4</sup> Calculation: if  $a$  grammes of Mohr's salt (=  $\frac{a}{7}$  grammes of iron) require  $b$  c.c. of permanganate solution, then 111.68:

$69.01 = \frac{a}{7} : x$ , or  $x = \frac{69.01a}{111.68 \times 7}$  grammes of  $\text{NaNO}_2$ , which are equivalent to  $a$  grammes of Mohr's salt or  $b$  c.c. of permanganate solution. Hence 1 c.c. of permanganate solution  $= \frac{69.01a}{111.68 \times 7 \times b}$  grammes of  $\text{NaNO}_2$ . If now  $c$  c.c. of permanganate solution are required in the titration of the nitrite, then in the volume of nitrite solution used there are  $\frac{69.01 \times a \times c}{111.68 \times 7 \times b}$  grammes of  $\text{NaNO}_2$ , from which the percentage strength of the solid nitrite may be calculated.

If a 1 per cent. nitrite solution (10 grammes in 1,000 c.c.) be used instead of the above, the calculation is simpler—1 c.c. of permanganate solution  $= 0.00345$  gramme of  $\text{NaNO}_2$ .

*Application.* For the so-called diazotised colours, "ice" colours, developed colours, etc. In dyeing and calico printing several of these colouring matters are largely used (*e.g.*, paranitraniline red).

**Sodium Phosphate**,  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O} = 358$ , solubility, cold water  $= 3 : 100$ , hot water  $= 96 : 100$ .

Also known as secondary or neutral sodium phosphate. It is often contaminated with sodium chloride, sulphate and carbonate. Its value depends on the percentage of phosphoric acid and the basicity.

*Phosphoric Acid.* 25 grammes are dissolved to 1,000 c.c., in 10 or 20 c.c. the phosphoric acid is precipitated with magnesia mixture and ammonia, the precipitate (magnesium ammonium phosphate) filtered off after twelve hours, washed with ammoniacal water, dried, ignited and weighed as magnesium pyrophosphate,  $\text{Mg}_2\text{P}_2\text{O}_7$ .

For the volumetric determination of phosphoric acid by means of uranium solution, see Fresenius, *Quant. Anal.*, 11, 545; *Zeits. anal. Chem.*, 1897, xxxvi., 81; *J. S. C. I.*, 1897, 262.

*Basicity.*—If the salt gives an alkaline reaction with phenolphthalein it contains more alkali than is required by the formula  $\text{Na}_2\text{HPO}_4$ , the excess of alkali may be titrated by normal acid, using phenolphthalein as indicator. If no coloration is given by phenolphthalein, there is present the neutral salt alone or a mixture of  $\text{Na}_2\text{HPO}_4$  and  $\text{NaH}_2\text{PO}_4$ , the latter of which may be estimated by titration with

caustic soda and phenolphthaleïn, the former by titration with acid and methyl orange.

*Application.*—In Turkey red dyeing instead of cow and sheep dung (which are now almost entirely replaced by sodium phosphate, arsenate and silicate); with wood colours (a more brilliant black); in silk-dyeing for weighting and to fix the tin and iron (4° to 6° B.) instead of, or together with soda; sodium phosphate is better than soda for weighting purposes, but it does not make the fibre voluminous, and overloading the fibre with phosphoric acid may be harmful. In dyeing with azo dye-stuffs. In recent years ammonium phosphate has been successfully employed in place of the sodium salt.

**Water Glass, Potassium or Sodium Silicate,**  $K_2Si_2O_7$  = mol. wt. 335.4,  $Na_2Si_2O_7$  = 303.2.

Since water glass frequently comes into commerce in solution, its value may be directly determined by means of the hydrometer; the silica may also be estimated (Fresenius, *Quant. Anal.*, I. 347). About 50 grammes are dissolved to 1,000 c.c., 50 c.c. of the solution repeatedly evaporated with hydrochloric acid and then heated for some hours at 110° C. The silicic acid then becomes insoluble, it is moistened with hydrochloric acid, filtered off, dried, ignited and weighed as  $SiO_2$ .

Silicic acid may also be determined acidimetrically by conversion into potassium fluosilicate (Stolba, *Zelts. anal. Chem.*, iv., 163), or directly titrated, with methyl orange as indicator, by normal acid.

Commercial water glass frequently contains a considerable excess of caustic soda, which would be very harmful to animal fibres and should therefore not be present; caustic soda would also have a solvent action on alumina mordants.

*Application.*—Similar to sodium phosphate; also in bleaching with hydrogen peroxide (instead of ammonia); in silk-dyeing in place of borax (alkali blue, logwood); as a mordant for cotton (water glass +  $H_2SO_4$  gives  $SiO_2$ , which fixes basic dyes); for fire-proofing fabrics; as an addition to soap; as an addition to varnishes; for dressing cotton warp; in printing, as a substitute for albumin; in finishing; as a fixing agent

for alumina mordants and tin (silk); to produce lustrous and tensile effects; since 1893 used in silk-dyeing to produce the important zinc phosphate-silicate weighting.

**Sodium Arsenate**,  $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$  = mol. wt. 402; solubility, cold water = 28 : 100, very soluble in hot water.

It must be free from nitric acid, not contain much lime, and at most contain 1 per cent. of  $\text{As}_2\text{O}_3$ .

The *basicity* may be estimated by direct titration with normal acid and methyl orange, supposing that no other acids are present. 1 c.c. of normal acid = 0.312 gramme of  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ .

*Arsenic Acid*.—0.5 gramme of the sample is precipitated as magnesium ammonium arsenate (Fresenius, *Quant. Anal.*, I. 283), the precipitate brought on to a weighed filter, dried at 100° C. and weighed. The precipitate may also be ignited and estimated as magnesium pyro-arsenate.

Having regard to the restricted use of this salt, the various methods of estimation are not described, the principle of the method given by Sutton (*Volumetric Analysis*, sixth ed.) may be mentioned—the arsenic acid is reduced to arsenious acid and the latter titrated with iodine solution.

*Arsenious acid* is determined by a reversal of the process for chlorine and iodine by means of sodium arsenite (see *Bleaching Powder*). 5 to 10 grammes of the arsenate are dissolved, bicarbonate solution added and the liquid titrated with  $\frac{1}{10}$  N iodine solution, 1 c.c. of which = 0.004948 gramme of  $\text{As}_2\text{O}_3$ . More than 1 per cent. of arsenious acid should not be present (see Christensen, *Zeits. anal. Chem.*, 1897, xxxvi, 81; *J. S. C. I.*, 1897, 262).

*Application*.—Restricted on account of its poisonous nature, otherwise similar to sodium phosphate.

**Sodium Tungstate**,  $\text{Na}_6\text{W}_7\text{O}_{21} \cdot 14\text{H}_2\text{O}$  = mol. wt. 2098, has now little interest. The tungstic acid may be determined by the method given by Fresenius (*Quant. Anal.*, II. 427). On account of the unimportance of the compound, the method is not described here.

According to H. Silbermann (*Patentzeit.*, 1897, No. 5, 70) the tungstic acid is estimated by precipitating the solution of a weighed quantity of sodium tungstate with

excess of hydrochloric acid, digesting for some hours at  $30^{\circ}$  to  $40^{\circ}$  C., washing the precipitate first with dilute hydrochloric acid, then with water, drying at  $105^{\circ}$  C. and weighing.

*Application.*— It possesses historic interest as an oxidising agent (instead of copper sulphide), chromium tungstate was also used; also as a weighting agent for silk, fixed upon the fibre as iron or tin tungstate.

**Sodium Stannate, Preparing Salt,**  $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$  = mol. wt. 266.7, 44.4 per cent. of tin.

Commercial sodium stannate contains 30 to 44 per cent. of stannic oxide; the impurities are caustic soda, soda, common salt and iron, occasionally it is adulterated with arsenate and tungstate. It should dissolve with as little residue as possible, be free from iron and not be too alkaline.

The total alkali is determined by titration with normal acid and methyl orange.

T. Goldschmidt estimates the tin as follows: 50 grammes of the sample are dissolved to 500 c.c., 10 c.c. of the solution are reduced in the presence of hydrochloric acid. The separated tin is dissolved in the same flask in an atmosphere of carbon dioxide, by boiling and adding more hydrochloric acid. After cooling, the stannous chloride formed is determined by means of standard ferric chloride solution and potassium iodide (starch solution). The titration is also conducted whilst a current of carbonic acid is led into the flask.

*Application.*— As a mordant for azo dyestuffs ( $4^{\circ}$  to  $5^{\circ}$  B.), followed by a bath of neutralised alum (25 grammes of alum + 10 grammes of crystallised soda in 1,000 c.c.); it was formerly used for weighting silk, but has now been entirely replaced by stannic chloride; in printing on cotton and wool.

**Sodium Aluminate,**  $\text{Na}_2\text{Al}_2\text{O}_4$  = mol. wt. 164.2.

When this compound is titrated with acid and phenolphthalein (less well with litmus), the end-reaction appears when all the alkali is saturated and the alumina has separated; if methyl orange be used, the end-reaction occurs when the compound  $\text{Al}_2(\text{SO}_4)_3$  has been formed, and the separated alumina has redissolved. 20 grammes of sodium aluminate dissolved to 1,000 c.c.; 10 c.c. are titrated

quite hot (in order to avoid the influence of carbonic acid, if present) with  $\frac{1}{5}$  N hydrochloric acid and phenolphthalein until the colour disappears, methyl orange is then added and titration with the same acid continued until the red coloration appears. The difference gives the alumina. (See also Lunge, *Zeits. angew. Chem.*, 1890, 227, 293, *J. S. C. I.*, 1890, 767.) 1 c.c. of  $\frac{1}{5}$  N hydrochloric acid = 0.0062 gramme of  $\text{Na}_2\text{O}$  = 0.003407 gramme of  $\text{Al}_2\text{O}_3$ .

Example: 0.2 gramme of aluminate require 8.5 c.c. (phenolphthalein) and 15.35 c.c. (methyl orange) of  $\frac{1}{5}$  N hydrochloric acid, a total of 23.85 c.c. The

$$\text{Na}_2\text{O} = \frac{8.5 \times 0.0062 \times 100}{0.2} = 26.35 \text{ per cent., the}$$

$$\text{Al}_2\text{O}_3 = \frac{15.35 \times 0.003407 \times 100}{0.2} = 26.15 \text{ per cent.}$$

*Application* - Very restricted in calico-printing.

**Borax, Sodium Biborate**,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  = mol. wt. 382; solubility, cold water = 6 : 100, hot water = 200 : 100.

The boric acid is determined by titration with acid and methyl orange. 25 grammes are dissolved to 1,000 c.c. and 50 c.c. titrated with normal sulphuric acid and methyl orange until the red coloration appears. 1 c.c. of normal acid = 0.191 gramme of crystallised borax. Soda, sodium chloride and sulphate occur as impurities. The percentage of soda, which would be titrated along with the borax, must be deducted when it is appreciable (*Zeits. angew. Chem.*, 1896, xxii., 679, *Zeits. anal. Chem.*, 1897, 568).

*Application*. Instead of soda in fermenting logwood; in calico-printing, as a solvent for casein, in dyeing wool with alkali blue (10 per cent. of the weight of the wool, or 300 to 350 grammes per 100 litres of bath).

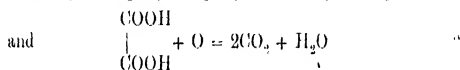
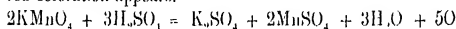
**Potassium Permanganate**,  $\text{KMnO}_4$  = mol. wt. 158; solubility, cold water = 6.45 : 100, very soluble in hot water.

The percentage of pure permanganate is determined volumetrically against oxalic acid or a ferrous salt. A solution of 6.32 grammes of pure permanganate in 1,000 c.c. would give a  $\frac{1}{10}$  N solution. Accordingly 20 c.c. of normal



oxalic acid, or 100 g.c. of  $\frac{1}{5}$  N oxalic acid, would require exactly 100 c.c. of the permanganate solution, if it were made from the chemically pure salt. The calculation is very simple: if 105 c.c. of permanganate are required instead of 100 c.c. for 100 c.c. of  $\frac{1}{5}$  N oxalic acid, then the permanganate is 94.85 per cent. pure ( $105 \cdot 100 = 100 \ x$ ,  $x = 94.85$ ).

The oxalic acid is strongly acidified with sulphuric acid and the titration conducted at 60° to 70° C. until a permanent red coloration appears.



(thus 2 mols. of permanganate correspond to 5 mols. of oxalic acid). The solution is standardised in a similar manner against a ferrous salt, *e.g.*, ferrous ammonium sulphate (Mohr's salt), 7 grammes of which = 1 gramme of iron;  $5\text{Fe} = 1\text{KMnO}_4$ ;  $2\text{FeO} + \text{O} = \text{Fe}_2\text{O}_3$ . 1 c.c. of  $\frac{1}{5}$  N permanganate solution = 0.0112 gramme of metallic iron = 0.0144 gramme of FeO = 0.016 gramme of  $\text{Fe}_2\text{O}_3$ .

*Application.*—In bleaching wool (neutral, alkaline or acid bath, best in a neutral bath of 1 : 1,000, since the bath may always be used again; in an alkaline bath the bleaching is slower, in an acid bath quicker). After bleaching, the material is washed with sulphurous acid, generally with an addition of sulphuric acid (occasionally 2 to 3 mols., otherwise the material may readily turn brown). Potassium permanganate cannot be used for bleaching silk, since the fibre is injured.

**Potassium Bichromate, Sodium Bichromate,**  $\text{K}_2\text{Cr}_2\text{O}_7$  = mol.-wt. 294.2; 68 per cent. of  $\text{CrO}_3$ ; solubility, cold water = 10.4 : 100; hot water = 1 : 1.  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  = 299; 67.19 per cent. of  $\text{CrO}_3$ ; more soluble than the potassium salt.

Potassium bichromate often contains potassium sulphate, sodium sulphate and normal chromate. Most important is the percentage of chromic acid.

*Total chromic acid* is determined by volumetric methods against ferrous ammonium sulphate. The solution of potas-

sium or sodium bichromate, acidified with sulphuric acid, is mixed with an excess of solution of ferrous ammonium sulphate, and the excess determined by adding  $\frac{1}{10}$  N bichromate solution until a drop of the solution no longer gives a blue coloration (Turnbull's blue) with potassium ferrieyanide on a porcelain plate.  $\text{CrO}_3 = 3\text{FeO}$ . Knecht, Rawson and Lowenthal give the following process: 5 grammes of the sample are dissolved to 1,000 c.c., and a burette filled with the solution. (In the case of the sodium salt it is better to dissolve 25 grammes to 500 c.c., and again dilute 100 c.c. to 1 litre.) 1 gramme of pure crystallised ferrous ammonium sulphate is weighed off, dissolved in a porcelain dish in a little water and 50 c.c. of 10 per cent. sulphuric acid added. The bichromate solution is added from the burette, with constant stirring, until a drop of the solution mixed with potassium ferrieyanide solution on a porcelain plate no longer gives a blue or greenish-blue coloration. 1 gramme of ferrous ammonium sulphate reduces 0.0853 gramme of  $\text{CrO}_3$ , therefore the volume of chromate solution added from the burette contains 0.0853 gramme of  $\text{CrO}_3$ .

Example: 5 grammes of  $\text{K}_2\text{Cr}_2\text{O}_7$  in 1,000 c.c.; 1 gramme of ferrous ammonium sulphate requires 25.2 c.c. of this solution;  $25.2 \div 0.0853 = 1,000 \times x, x = 3.385$  grammes of  $\text{CrO}_3$ ;  $5 \div 3.385 = 100 \times x, x = 67.70$  per cent. of  $\text{CrO}_3$ .

*Free chromic acid* is detected by means of the hydrogen peroxide reaction: 2.5 to 5 grammes of the bichromate are dissolved in 40 to 50 c.c. of water, 10 c.c. of hydrogen peroxide and 20 c.c. of ether added, and the whole mixed in a cylinder. In the presence of free chromic acid the ether layer becomes blue; the coloration rapidly disappears.

*Neutral chromate* is estimated by McCulloch by means of the above reaction (*Chem. News* 1887, iv. 2). As in the detection of free chromic acid, 2.5 to 5 grammes are dissolved in 40 to 50 c.c. of water and the solution shaken in a stoppered cylinder of 120 c.c. capacity with 10 c.c. of hydrogen peroxide and 20 c.c. of ether. Decinormal sulphuric acid is now added in small quantities at a time, with frequent shaking, until the ether acquires a pale blue colour. 1 c.c. of  $\frac{1}{10}$  N acid = 0.01003 gramme of  $\text{CrO}_3$  as normal chromate,

0.01623 gramme of  $\text{Na}_2\text{CrO}_4$  or 0.01943 gramme of  $\text{K}_2\text{CrO}_4$  in the quantity of material taken. The hydrogen peroxide and bichromate naturally should not contain free acid, any free acid they contain must be deducted.

*Bichromate.* (a) According to McCulloch the bichromate may be directly estimated by titration with normal caustic soda and phenolphthalein; the normal chromate may then be found by deducting the chromic acid present as bichromate from the total chromic acid. Since the end-reaction in titrating with caustic soda is ill defined, excess is added and titrated back with normal acid. 1 c.c. of  $\frac{1}{10}$  N caustic soda = 0.0100 gramme of  $\text{CrO}_3$  as bichromate.

(b) R. Thomson (*Chem. News*, 1885, lii., 29) titrates directly with lacmoid as indicator (see under *Indicators*), towards which bichromate is neutral, but normal chromate alkaline. The latter can accordingly be estimated by means of standard acid and lacmoid paper.

Example. 100 c.c. of 1 per cent. solution ( $\approx$  1 gramme) in titration with  $\frac{1}{10}$  N sulphuric acid and lacmoid required 12.6 c.c. of acid;  $0.0100 \times 12.6 \times 100 = 12.6$  per cent. of  $\text{CrO}_3$  as chromate. Total  $\text{CrO}_3 = 70.60$  per cent., therefore bichromate =  $70.60 - 12.6 = 58.00$  per cent. of  $\text{CrO}_3$  as bichromate.

*Application.* One of the most important salts used in dyeing. As a mordant for wool (with tartar, oxalic acid, sulphuric acid, lactic acid, etc.); in developing aniline black (dyeing and printing, also lead chromate in printing), in blue-printing; for fast browns from catechu; as an addition to bluestone black (logwood), which is thus made more resistant to alkalis; as a discharging agent in calico-printing; for chrome yellow, orange and olive in combination with the indigo vat as "Jager" green.

Sodium bichromate is hygroscopic, generally more impure contains more normal chromate— and requires more careful control, whilst the potassium salt is generally obtained in very good quality. Also the sodium salt is used with reluctance in printing, since the goods dry badly, in wool-dyeing, on the other hand, it is preferred because it is cheaper and more easily soluble.

**Vanadates.**—Ammonium vanadate  $(\text{NH}_4)_3\text{VO}_4$ , = mol. wt. 169. Vanadium chloride, blue vanadium solution (= vanadium tetra-, tri- and bichlorides).

The vanadates are evaluated by means of the proportion of vanadic acid, which can be determined (Fresenius, *Quant. Anal.*, II. 312) by precipitating ammonium vanadate by saturated ammonium chloride solution, when impurities remain in solution. The precipitate is filtered, ignited, and weighed as vanadic acid,  $\text{V}_2\text{O}_5$ . The most usual impurity is chromic acid.

*Application.*—As an oxidising agent in printing aniline black, in place of copper sulphide, which readily dries and causes streaks. It is active at extraordinary dilutions 0.2 gramme per kilo. of printing colour, excess may readily spoil the fabric. The blue vanadium solution is obtained by reducing vanadic acid with glycine in the presence of hydrochloric acid at water-bath temperatures (100 grammes of ammonium vanadate + 400 grammes of hydrochloric acid + 400 grammes of water, then a solution of about 50 grammes of glycine in 100 c.c. of water added, the mixture warmed until the blue coloration appears and finally diluted to 10 litres).

#### ALKALIS.

**Ammonia**,  $\text{NH}_3$ , = mol. wt. 17, solubility, cold water = 1,050 volumes : 1. The strength is estimated by means of the hydrometer, or better volumetrically. 50 grammes are diluted to 1,000 c.c. and 50 c.c. titrated with normal acid and litmus, etc. 1 c.c. = 0.017 g. of  $\text{NH}_3$ .

Ammonia solution should leave no residue on evaporation. The common impurities are sulphuric acid, sulphuric acid hydrogen, carbonic acid and chlorine. Ordinary technical ammonia = 16° B. = 9.9 per cent. of ammonia.

*Application.* For washing wool and shoddy dyed with alizarine (the dye becomes faster to rubbing); in bleaching with hydrogen peroxide; for precipitating lead on the fibre; instead of soda and fixed alkalis.

*Aqueous Ammonia Solution (Lunge).*

| Specific Gravity. | NH <sub>3</sub> per cent. | Specific Gravity. | NH <sub>3</sub> per cent. | Specific Gravity. | NH <sub>3</sub> per cent. | Specific Gravity. | NH <sub>3</sub> per cent. |
|-------------------|---------------------------|-------------------|---------------------------|-------------------|---------------------------|-------------------|---------------------------|
| 0.996             | 0.91                      | 0.968             | 7.82                      | 0.952             | 12.17                     | 0.924             | 20.49                     |
| 0.992             | 1.84                      | 0.961             | 8.81                      | 0.950             | 12.71                     | 0.920             | 21.75                     |
| 0.988             | 2.80                      | 0.962             | 9.35                      | 0.946             | 13.88                     | 0.916             | 23.03                     |
| 0.984             | 3.80                      | 0.960             | 9.91                      | 0.942             | 15.04                     | 0.910             | 24.99                     |
| 0.980             | 4.80                      | 0.958             | 10.47                     | 0.938             | 16.22                     | 0.900             | 28.33                     |
| 0.976             | 5.80                      | 0.956             | 11.03                     | 0.931             | 17.12                     | 0.890             | 31.75                     |
| 0.972             | 6.80                      | 0.954             | 11.60                     | 0.930             | 18.61                     | 0.882             | 34.95                     |

**Ammonium Salts.** Sulphate, acetate, oxalate.

The ammonia is estimated in the ordinary manner by distillation: 0.5 to 1 gramme of the sample is distilled with excess of caustic soda, the receiver contains a measured excess of normal acid, which is titrated, after the distillation, by normal caustic soda. 1 c.c. of N acid used = 0.017 gramme of NH<sub>3</sub> (Fresenius, *Quant. Anal.*, 1, 178).

*Application.*—Restricted on account of the high price. In dyeing with sulphonie acid dye-stuffs to secure better equalisation (induline).

**Sodium Hydroxide, Caustic Soda,** NaOH = mol. wt. 40; solubility, cold water = 60, 100, hot water = 210, 100.

Caustic soda comes into the market both solid and in solution, the latter at strengths of 30°, 36° and 39° B. The value is given by the percentage of sodium hydroxide, which can be determined in solutions approximately by means of the hydrometer, more accurately by titration. Caustic soda should, as far as possible, be free from carbonate, thus an estimation of sodium carbonate is important. Either the caustic soda alone is determined, or the carbonate also.

*Total Alkali.*—25 grammes are dissolved to 1,000 c.c. and 100 c.c. titrated with N acid and methyl orange, phenolphthalein, etc. Also, although more complicated, excess of acid may be added, the liquid boiled for 5 minutes and titrated back with N caustic soda, litmus or phenolphthalein being the indicator. 1 c.c. of normal acid = 0.04 gramme of NaOH or 0.031 gramme of Na<sub>2</sub>O.

*Specific Gravity of Caustic Soda Solutions at 15° (Lunge).*

| Specific Gravity. | Degrees Baumé. | Degrees Twaddell. | Na <sub>2</sub> O per cent. | NaOH per cent. | 1 cub. metre contains    |             |
|-------------------|----------------|-------------------|-----------------------------|----------------|--------------------------|-------------|
|                   |                |                   |                             |                | Na <sub>2</sub> O kilos. | NaOH kilos. |
| 1·007             | 1              | 1·4               | 0·17                        | 0·61           | 1                        | 6           |
| 1·011             | 2              | 2·8               | 0·33                        | 1·20           | 9                        | 12          |
| 1·022             | 3              | 4·1               | 1·55                        | 2·00           | 16                       | 21          |
| 1·029             | 4              | 5·8               | 2·10                        | 2·71           | 22                       | 28          |
| 1·036             | 5              | 7·2               | 2·60                        | 3·35           | 27                       | 35          |
| 1·045             | 6              | 9·0               | 3·10                        | 4·00           | 32                       | 42          |
| 1·052             | 7              | 10·1              | 3·60                        | 4·61           | 38                       | 49          |
| 1·060             | 8              | 12·0              | 4·10                        | 5·29           | 43                       | 56          |
| 1·067             | 9              | 13·1              | 4·55                        | 5·87           | 49                       | 63          |
| 1·075             | 10             | 15·0              | 5·08                        | 6·55           | 55                       | 70          |
| 1·083             | 11             | 16·6              | 5·67                        | 7·31           | 61                       | 79          |
| 1·091             | 12             | 18·2              | 6·20                        | 8·00           | 68                       | 87          |
| 1·100             | 13             | 20·0              | 6·73                        | 8·68           | 74                       | 95          |
| 1·108             | 14             | 21·6              | 7·30                        | 9·42           | 81                       | 104         |
| 1·116             | 15             | 23·2              | 7·80                        | 10·06          | 87                       | 112         |
| 1·125             | 16             | 25·0              | 8·50                        | 10·97          | 96                       | 123         |
| 1·134             | 17             | 26·8              | 9·18                        | 11·81          | 101                      | 131         |
| 1·142             | 18             | 28·1              | 9·80                        | 12·64          | 112                      | 144         |
| 1·152             | 19             | 30·1              | 10·50                       | 13·55          | 121                      | 156         |
| 1·162             | 20             | 32·4              | 11·14                       | 14·37          | 129                      | 167         |
| 1·171             | 21             | 34·2              | 11·73                       | 15·13          | 137                      | 177         |
| 1·180             | 22             | 36·0              | 12·33                       | 15·91          | 146                      | 188         |
| 1·190             | 23             | 38·0              | 13·00                       | 16·77          | 155                      | 200         |
| 1·200             | 24             | 40·0              | 13·70                       | 17·67          | 164                      | 212         |
| 1·210             | 25             | 42·0              | 14·40                       | 18·58          | 171                      | 225         |
| 1·220             | 26             | 44·0              | 15·18                       | 19·58          | 185                      | 239         |
| 1·231             | 27             | 46·2              | 15·96                       | 20·59          | 196                      | 253         |
| 1·241             | 28             | 48·2              | 16·76                       | 21·42          | 208                      | 266         |
| 1·252             | 29             | 50·4              | 17·55                       | 22·64          | 220                      | 283         |
| 1·263             | 30             | 52·6              | 18·35                       | 23·67          | 232                      | 299         |
| 1·274             | 31             | 54·8              | 19·23                       | 24·81          | 245                      | 316         |
| 1·285             | 32             | 57·0              | 20·00                       | 25·80          | 257                      | 332         |
| 1·297             | 33             | 59·1              | 20·80                       | 26·83          | 270                      | 348         |
| 1·308             | 34             | 61·6              | 21·55                       | 27·80          | 282                      | 364         |
| 1·320             | 35             | 64·0              | 22·35                       | 28·83          | 295                      | 381         |
| 1·332             | 36             | 66·4              | 23·20                       | 29·91          | 309                      | 399         |
| 1·345             | 37             | 69·0              | 24·20                       | 31·22          | 326                      | 420         |
| 1·357             | 38             | 71·4              | 25·17                       | 32·47          | 342                      | 441         |
| 1·370             | 39             | 74·0              | 26·12                       | 33·69          | 359                      | 462         |
| 1·383             | 40             | 76·6              | 27·10                       | 34·96          | 375                      | 483         |
| 1·397             | 41             | 79·4              | 28·10                       | 36·25          | 392                      | 506         |
| 1·410             | 42             | 82·0              | 29·05                       | 37·47          | 410                      | 528         |
| 1·424             | 43             | 84·8              | 30·08                       | 38·80          | 428                      | 553         |
| 1·438             | 44             | 87·6              | 31·00                       | 39·99          | 446                      | 575         |
| 1·453             | 45             | 90·6              | 32·10                       | 41·41          | 466                      | 602         |
| 1·468             | 46             | 93·6              | 33·20                       | 42·83          | 487                      | 629         |
| 1·483             | 47             | 96·6              | 34·40                       | 44·38          | 510                      | 658         |
| 1·498             | 48             | 99·6              | 35·70                       | 46·15          | 535                      | 691         |
| 1·514             | 49             | 102·8             | 36·90                       | 47·60          | 559                      | 721         |
| 1·530             | 50             | 108·0             | 38·00                       | 49·02          | 581                      | 750         |

*Caustic Alkali.*—To a second 100 c.c. excess of neutral barium chloride solution is added to precipitate the carbonate, and the mixture titrated (without filtering) with normal acid and methyl orange or litmus to incipient red coloration. 1 c.c. of N acid = 0.04 gramme of NaOH or 0.031 gramme of  $\text{Na}_2\text{O}$  as free caustic soda.

*Sodium Carbonate.*—The difference between the total alkali and caustic alkali gives the carbonate. The amount of free and caustic alkali can also be estimated by titrating first with N acid and phenolphthalein which gives the whole of the caustic and half the carbonate, then finishing the titration with methyl orange which gives the other half of the carbonate.

Commercial caustic soda generally contains much common salt, sodium sulphate and excess of water.

*Application*—Restricted. In the preparation of Turkey red oil, for washing and bleaching purposes, in printing indigo; as an addition to the potassium ferrieyanide oxidising mass. Caustic potash, since it is dearer and without special advantage, is hardly used in the textile industries. See also *Zeits. angew. Chem.*, 1896, 455.

*Lime.*—Quicklime,  $\text{CaO}$  = 56, solubility, cold water = 1.778; hot water = 1.1,270. Slaked lime  $\text{Ca(OH)}_2$  = 74.

The amount of calcium oxide is best estimated by the process given by Degener: 100 grammes of quicklime are completely slaked, the paste brought into a 500 c.c. flask, the liquid filled up to the mark, and after shaking, 100 c.c. withdrawn with a pipette. This 100 c.c. is again diluted to 1,000 c.c., well shaken, and 25 c.c. brought into a porcelain dish. A few grains of precipitated calcium carbonate are then added and alcoholic phenacetolm solution; normal acid is now added, under constant stirring, until the liquid where the acid drops in, which becomes yellow, at once turns red again. When the red coloration does not appear until after some seconds, the volume of acid used is read off, and two more drops added. If the liquid now remains yellow the previous reading was correct, but if it again becomes red, the reading was premature and the addition of acid must be continued. 1 c.c. of N acid = 0.0283 gramme of  $\text{CaO}$ .

The powder formed on slaking should be fine, and pulverulent, feel soft, and when stirred with a small quantity of water should give a smooth, "fat," and slippery paste. If this is not the case the lime is bad, "lean," and contains much magnesia and alumina.

*Application.*—In vat-dyeing to dissolve the indigo; in black cotton-dyeing (the cheapest black); practically no longer used for bleaching, to strip wood colour from wool, etc.

**Sodium Carbonate, Soda,** Calcined soda,  $\text{Na}_2\text{CO}_3$  : mol. wt. 106; solubility, cold water = 7–100, hot water 45–100. Crystallised soda or soda crystals  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  = 286, solubility, cold water = 21.3–100, hot water 420–100.

Soda is usually contaminated by sulphate, chloride, sulphite, alkaline sulphide (see sodium nitroprusside), lime, iron and free caustic soda. Most important are estimations of the total alkali and caustic soda.

*Total Alkali.*—The estimation is conducted as in caustic soda: 25 to 50 grammes are dissolved to 1,000 c.c. (25 grammes of calcined, 50 grammes of crystallised soda) and 50 c.c. of the solution titrated with N acid, methyl orange being the indicator. 1 c.c. of N acid = 0.031 gramme of  $\text{Na}_2\text{O}$  = 0.053 gramme of  $\text{Na}_2\text{CO}_3$  = 0.143 gramme of  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ . The value obtained corresponds to the total alkali, from which the caustic alkali, if determinable, is to be deducted.

*Caustic Alkali.*—Excess of barium chloride solution is added to a second 50 c.c. and the solution tested, after a few minutes, for alkaline reaction. If it is alkaline, it is titrated with  $\frac{1}{10}$  N hydrochloric or sulphuric acid, and methyl orange (or litmus) to acid reaction. 1 c.c. of  $\frac{1}{10}$  N acid = 0.0031 gramme of  $\text{Na}_2\text{O}$  (see also *Caustic Soda*, p. 75).

*Sodium Carbonate.*—The difference between the total and caustic alkali gives the soda present as carbonate.

Bicarbonate, which may be present, in absence of caustic soda is not generally estimated, since it does not produce any inconveniences. The iron is often harmful; it is best estimated by colorimetric methods. (Estimation of bicarbonate, see Lunge, *Handbuch der Sodaindustrie*, ii., 648;



Bockmann, *Chemisch-technische Untersuchungen*, i., 390, 391).

*Application*.--In wool washing to remove grease (caustic alkali harmful); in calico-bleaching; in linen-bleaching; for fixing metallic oxides on the fibre (*e.g.*, tin oxides on silk); in alizarine-dyeing for softening and fixing alumina and chromium oxide on the fibre; to neutralise alum (Turkey red); in dyeing cotton with bluestone (logwood) black; in dyeing with the benzidine dyes, etc.

For the same reason that caustic potash is not used, the dearer potassium carbonate (potashes) has no advantages over soda, which would justify its employment.

**Calcium Carbonate, Chalk**,  $\text{Ca}(\text{O})_2$  = 100; solubility, cold water = 1 : 10,600; hot water = 1 : 8,834.

The pure compound is found in commerce. The proportion of calcium carbonate may be estimated as in soda; an excess of acid is naturally added, which is titrated back. Since a solution cannot be made, 2 grammes are weighed off, 50 c.c. of N acid cautiously added (the substance should previously be covered with water), the carbonate carefully dissolved and the solution titrated, with or without previous boiling to drive off carbonic acid, by means of N caustic soda and phenolphthalein or methyl orange respectively. 1 c.c. of N acid = 0.05 gramme of  $\text{Ca}(\text{O})_2$ .

*Application* restricted. For fixing metallic oxides (Turkey red dyeing); for sumach black; for removing traces of acid from fabrics, etc.

#### PEROXIDES.

**Hydrogen Peroxide**,  $\text{H}_2\text{O}_2$  = mol. wt. 34; very readily soluble in water. The value of the solution depends on the percentage of hydrogen peroxide and the absence of mineral acids—hydrochloric and sulphuric. It generally comes into commerce as a 3 per cent. solution, the strength of which is estimated by one of the following processes:—

1. With permanganate. 10 c.c. of the solution are diluted, 30 c.c. of sulphuric acid (1 : 3) added and the liquid titrated in the cold by potassium permanganate, until the red color-

tion is just permanent. 1 c.c. of  $\frac{1}{5}$  N permanganate = 0.0034 gramme of  $\text{H}_2\text{O}_2$  = 0.0016 gramme of O.

II. By means of potassium iodide and thiosulphate (see Kingzett, *Journ. Chem. Soc.*, 1880, 792). 10 c.c. are mixed with 30 c.c. of dilute sulphuric acid and excess of potassium iodide. After five minutes the liberated iodine is determined by titration with  $\frac{1}{10}$  N thiosulphate solution and starch, until the blue coloration disappears. 1 c.c. of  $\frac{1}{10}$  N thiosulphate = 0.0017 gramme of  $\text{H}_2\text{O}_2$  = 0.0008 gramme of O. (1 gramme of oxygen at 0° C. and 760 mm. pressure occupies 697.5 c.c.).

III. Coulamine recommends a more complicated gasometric estimation, unsuitable for technical purposes (*Dingler's Polyt. Journ.*, 1888, 267, 238).

The solution should also be examined for residue, hydrochloric acid and especially sulphuric acid.

*Application.* For bleaching tussur, chappe,<sup>1</sup> pure and mixed silk fabrics, wool and jute, also in combination with sulphurous acid (first  $\text{H}_2\text{O}_2$ , then  $\text{SO}_2$ , or the reverse), as an oxidising agent it has not yet found application in the textile industries. As a bleaching agent it is being supplanted by sodium peroxide.

**Barium Peroxide**,  $\text{BaO}_2$ : mol. wt. 169.4; insoluble in cold, decomposed by hot water.

The peroxide always contains much monoxide, the value is determined by the proportion of peroxide. This is best estimated as follows (*Zeits. anal. Chem.*, 1892, xxxi., 28): 0.3 gramme of barium peroxide is suspended in 500 c.c. of water and then dissolved by the addition of 10 c.c. of hydrochloric acid; 10 c.c. of 20 per cent. manganous sulphate solution are next added and the liquid titrated by  $\frac{1}{5}$  N permanganate, 1 c.c. of which = 0.01694 gramme of  $\text{BaO}_2$ . In order to obtain a good average result, it is necessary to perform at least three to four titrations and take the mean. Good technical barium peroxide should contain at least 80 per cent. of  $\text{BaO}_2$ .

<sup>1</sup> A term used on the Continent for silk waste which has not been boiled to remove the gum.

*Application.*—As a bleaching agent, followed by a bath of hydrochloric acid, (most suitable for tussur, chappe and various woollen materials). •Wool generally loses in elasticity by treatment with hydrogen peroxide (5 to 10 per cent. of barium peroxide suspended in water, the materials left in for one to two hours and then given a dilute hydrochloric acid bath). The action is rather more energetic than that of ready-made hydrogen peroxide, since the latter substance comes into action *in statu nascendi*.

**Sodium Peroxide**,  $\text{Na}_2\text{O}_2$  = mol. wt. 78; decomposed by water. The proportion of sodium peroxide is determined in a similar manner to barium peroxide. The weighing and other operations must be conducted more quickly and carefully, since sodium peroxide is rapidly decomposed in moist air. The peroxide must also be dissolved in a large volume of dilute sulphuric acid (about equal to that of the hydrochloric acid mentioned above), otherwise loss occurs; the solution is then titrated as above with  $\frac{1}{2}$  N permanganate, 1 c.c. of which = 0.0078 gramme of  $\text{Na}_2\text{O}_2$ .

*Application.*—Has already found extensive application as a bleaching agent. Especially suitable for chappe, tussur and straw.

**Zinc Dust**, Zn = atom. wt. 65.4; insoluble in water.

Zinc dust should contain no grains which can be seen or felt by the fingers, it should feel uniformly dusty. Also it should not contain too much iron and zinc oxide, the usual impurities. The proportion of metallic zinc is estimated by means of its reducing properties (see also Drewson, *Zeits. Anal. Chem.*, xix., 50, and Fresenius, *Quant. Anal.*, 11. 288). 10 grammes of zinc dust are brought into a conical flask with 40 grammes of potassium bichromate and 300 c.c. of water, 150 c.c. of sulphuric acid (1 : 5) are gradually added during three to four hours with frequent stirring on the water-bath. The addition of acid must be so regulated that no evolution of hydrogen is perceptible throughout, *i.e.*, the whole of the hydrogen produced must reduce the bichromate whilst *in statu nascendi*; 5 to 10 c.c. (as a maximum) of acid are added every ten minutes. When the zinc is completely dissolved the solution is diluted to 1,000 c.c. and 100 c.c.

titrated with a solution of ferrous ammonium sulphate (70 : 500) standardised against bichromate solution (15 : 1,000), until a drop of the mixture begins to give a blue coloration with potassium ferricyanide on a porcelain plate. About 150 c.c. of ferrous solution will be required, this corresponds to about 90 per cent. of metallic zinc, which is the percentage in good zinc dust.

The weight of the potassium bichromate, multiplied by 0.6650, gives the equivalent weight of zinc, or 1 c.c. of N bichromate solution = 0.03268 gramme of Zn. ( $3\text{Zn} + 7\text{H}_2\text{SO}_4 + \text{K}_2\text{Cr}_2\text{O}_7 = \text{Cr}_2(\text{SO}_4)_3 + 3\text{ZnSO}_4 + \text{K}_2\text{SO}_4 + 7\text{H}_2\text{O}$ ;  $3\text{Zn} = 1\text{K}_2\text{Cr}_2\text{O}_7$  or  $196.14 \text{ Zn} = 998 \text{ K}_2\text{Cr}_2\text{O}_7$ .)

•Knecht and Rawson work in the following manner: 0.665 gramme of zinc dust (the same quantity of pure zinc would reduce exactly 1 gramme of  $\text{K}_2\text{Cr}_2\text{O}_7$ ) is mixed with 80 c.c. of a bichromate solution containing 25 grammes in 1 litre, and with 10 c.c. of dilute sulphuric acid, after ten to fifteen minutes, a second similar quantity of acid is added and later a third, stirring from time to time. Then 20 c.c. of strong sulphuric acid are added and an excess (about 10 grammes) of pure ferrous ammonium sulphate. After mixing, a drop of the solution must give a blue coloration with potassium ferricyanide, otherwise more ferrous salt must be added. The excess of ferrous salt is then titrated by N bichromate solution. The quantity of bichromate, reduced by 0.665 gramme of the sample, when multiplied by 100 gives immediately the percentage of metallic zinc. Any iron present will be included in the zinc. The weight of pure zinc is found by multiplying by 0.665 the weight of the bichromate reduced by it; in calculating in this manner it is not necessary to weigh off exactly a definite quantity of zinc dust.

<sup>1</sup>The calculation is evidently based upon a method of operation slightly different to that described in the previous paragraph, namely, that to the 100 c.c. of solution, after reduction of the bichromate by the zinc dust, an excess (c.c.) of ferrous ammonium sulphate solution is added and the excess titrated by adding f.c.c. of bichromate solution until the blue coloration with potassium ferricyanide is no longer given. —(TRANSLATOR).

Example<sup>1</sup>: 0.665 gramme of zinc dust; 80 c.c. of bichromate solution (25:1,000); 10 grammes of ferrous ammonium sulphate; 6.1 c.c. of bichromate solution in titrating back / 1 gramme of the ferrous salt = 0.1253 gramme of  $K_2Cr_2O_7$ ;  $0.025 \times 86.1 = 2.1525$  = total  $K_2Cr_2O_7$ ;  $0.1253 \times 10 = 1.253$  grammes of  $K_2Cr_2O_7$  reduced by the ferrous salt;  $2.1525 - 1.253 = 0.8995$  gramme of  $K_2Cr_2O_7$  reduced by the zinc;  $0.8995 \times 100 = 89.95$  per cent. of metallic zinc. Or 0.662 gramme of zinc dust = 0.8995 gramme of  $K_2Cr_2O_7$ ,  $0.8995 \times 0.6619 = 0.5957$  gramme of metallic zinc in 0.662 gramme of the sample, hence 89.95 per cent. of metallic zinc.

Liebschutz first withdraws the iron from 1 gramme of the sample by means of a magnet, and then treats with a warm neutral solution of 15 grammes of copper sulphate. After standing some time the oxide is removed by dilute sulphuric acid, the separated metallic copper washed with water, dissolved in nitric acid and titrated by normal potassium cyanide solution. The weight of the copper so found, multiplied by 1.028, gives the weight of metallic zinc in the quantity taken.

The metallic zinc may also be estimated gasometrically by means of the volume of hydrogen evolved on treating the zinc dust with dilute hydrochloric or sulphuric acid.

*Application.*— As a reducing agent and resist in calico-printing; in indigo-dyeing (hydrosulphite vat).

## CHAPTER IV.

### ORGANIC COMPOUNDS.

#### FATTY ACIDS AND THEIR SALTS.

**Acetic Acid**,  $\text{CH}_3\cdot\text{CO}\cdot\text{OH}$  mol. wt. 60, miscible with water in every proportion.

Acetic acid comes into commerce in the most varied degrees of purity. The principal impurities are hydrochloric and sulphuric acids (especially harmful in printing), iron, lead, lime, sulphurous acid and empyrenumatic substances. The strength is estimated by titration—50 grammes are diluted to 1,000 c.c. and 50 c.c. of the solution titrated with N caustic soda and phenolphthalein, 1 c.c. of N soda = 0.06 gramme of anhydrous acetic acid. Crude, highly coloured acid frequently cannot be titrated directly; in this case litmus paper must be used as indicator or Mohr's process employed. Mohr treats 5 grammes of acetic acid at the boiling point with a weighed excess of calcium carbonate, filters, washes the residue with hot water and estimates the undecomposed carbonate by titration (excess of nitric acid titrated back by N soda), from which the proportion of acetic acid can be calculated. In addition the residue on evaporation at  $110^\circ\text{C}$ . may be estimated; very little should remain. If free sulphuric acid is present, it can be extracted by alcohol from the evaporated residue (sulphates are precipitated), the solution filtered, diluted and titrated with  $\frac{1}{10}$  N soda or estimated gravimetrically by means of barium chloride.

*Application.*—Added to the printing colour, in the proportion of about 50 grammes of acetic acid of  $4^\circ\text{B.}$  to 1 kilo. in order to prevent the formation of lakes before printing; in

dyeing with dyes sensitive to acids (*e.g.* eosine); for brightening silk; in wool-dyeing to correct calcareous waters; for thick woollen materials to secure more equal dyeing and better dyeing throughout (also as ammonium salt); as an addition to ferric acetate.

*Specific Gravity of Acetic Acid at 15° C. (Oudemans).*

| Specific Gravity | Acetic Acid per cent. | Specific Gravity | Acetic Acid per cent. | Specific Gravity | Acetic Acid per cent. | Specific Gravity | Acetic Acid per cent. |
|------------------|-----------------------|------------------|-----------------------|------------------|-----------------------|------------------|-----------------------|
| 0.9992           | 0                     | 1.0363           | 26                    | 1.0631           | 52                    | 1.0748           | 77                    |
| 1.0007           | 1                     | 1.0375           | 27                    | 1.0638           | 53                    | 1.0748           | 78                    |
| 1.0022           | 2                     | 1.0388           | 28                    | 1.0646           | 54                    | 1.0748           | 79                    |
| 1.0037           | 3                     | 1.0400           | 29                    | 1.0653           | 55                    | 1.0748           | 80                    |
| 1.0052           | 4                     | 1.0412           | 30                    | 1.0660           | 56                    | 1.0747           | 81                    |
| 1.0067           | 5                     | 1.0421           | 31                    | 1.0666           | 57                    | 1.0746           | 82                    |
| 1.0083           | 6                     | 1.0436           | 32                    | 1.0673           | 58                    | 1.0744           | 83                    |
| 1.0098           | 7                     | 1.0447           | 33                    | 1.0679           | 59                    | 1.0742           | 84                    |
| 1.0113           | 8                     | 1.0459           | 34                    | 1.0685           | 60                    | 1.0739           | 85                    |
| 1.0127           | 9                     | 1.0470           | 35                    | 1.0691           | 61                    | 1.0736           | 86                    |
| 1.0142           | 10                    | 1.0481           | 36                    | 1.0697           | 62                    | 1.0731           | 87                    |
| 1.0157           | 11                    | 1.0492           | 37                    | 1.0702           | 63                    | 1.0726           | 88                    |
| 1.0171           | 12                    | 1.0502           | 38                    | 1.0707           | 64                    | 1.0720           | 89                    |
| 1.0185           | 13                    | 1.0513           | 39                    | 1.0713           | 65                    | 1.0713           | 90                    |
| 1.0200           | 14                    | 1.0523           | 40                    | 1.0717           | 66                    | 1.0705           | 91                    |
| 1.0214           | 15                    | 1.0533           | 41                    | 1.0721           | 67                    | 1.0696           | 92                    |
| 1.0228           | 16                    | 1.0543           | 42                    | 1.0725           | 68                    | 1.0686           | 93                    |
| 1.0242           | 17                    | 1.0552           | 43                    | 1.0729           | 69                    | 1.0674           | 94                    |
| 1.0256           | 18                    | 1.0562           | 44                    | 1.0733           | 70                    | 1.0660           | 95                    |
| 1.0270           | 19                    | 1.0571           | 45                    | 1.0737           | 71                    | 1.0644           | 96                    |
| 1.0284           | 20                    | 1.0580           | 46                    | 1.0740           | 72                    | 1.0625           | 97                    |
| 1.0298           | 21                    | 1.0589           | 47                    | 1.0742           | 73                    | 1.0604           | 98                    |
| 1.0311           | 22                    | 1.0598           | 48                    | 1.0744           | 74                    | 1.0580           | 99                    |
| 1.0324           | 23                    | 1.0607           | 49                    | 1.0746           | 75                    | 1.0553           | 100                   |
| 1.0337           | 24                    | 1.0615           | 50                    | 1.0747           | 76                    |                  |                       |
| 1.0350           | 25                    | 1.0623           | 51                    |                  |                       |                  |                       |

*Note.*—The specific gravities above 1.0553 correspond to two solutions of very different strengths. In order to ascertain whether the acid under examination has a greater strength than acid of the maximum density (78 per cent.), a little water is added; if the specific gravity is increased, the acid was stronger than 78 per cent.; if the specific gravity is decreased, the acid was weaker than 78 per cent.

**Acetates** are tested for the ordinary impurities, sulphate, chloride, iron, lead, lime, etc. An estimation of acetic acid is generally unnecessary; it is simpler to estimate the metal, as, *e.g.*, in chromium acetate. It is necessary also to examine for excess of free acid or mineral acid (basicity) and complete solubility. If it is necessary to estimate acetic acid, a weighed quantity of the acetate is distilled with phosphoric acid and the distillate titrated. For example, 5 grammes of acetate of lime are distilled almost to dryness with 50 c.c. of water and 50 c.c. of phosphoric acid (specific gravity 1.2) from a retort provided with a Liebig's condenser, the contents of the retort are diluted with 50 c.c. of water and again distilled; a third distillation is similarly performed. In the distillate, or in an aliquot portion, the acetic acid is estimated by N caustic soda, 1 c.c. = 0.06 gramme of acetic acid = 0.079 gramme of anhydrous calcium acetate (Fresenius, *Quant. Anal.*, II. 201). The acetates or their solutions are frequently made by the consumer, in which case the materials must be tested.

*Sodium acetate* is used in calico-printing and wool-dyeing.

*Calcium acetate* in printing alizarine red, an important raw material for various preparations of acetic acid. It should be 90 per cent. pure.

*Lead acetate, sugar of lead*, contains as impurities calcium acetate, lime, lead carbonate; is used for chrome yellow and orange; hardly ever used now for weighting raw silk.

*Aluminium Acetate, "Red Mordant"*.—In Turkey red dyeing (1° to 8° B.) in a similar manner to aluminium sulphocyanide and sulphate; for fixing wood colours in printing; for mordanting silk, for softening chappe (see footnote, p. 83); for water-proofing.

*Tin acetate* is used to discharge azo-dyestuffs in calico-printing.

*Chromium acetate* in printing alizarine colours (generally chromous acetate) instead of pyrolignite of iron.

*Copper acetate* (normal copper acetate or verdigris =  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ ) is used in blue printing and in calico-printing to fix logwood. "French verdigris" is the basic salt  $\text{Cu}_2(\text{C}_2\text{H}_3\text{O}_2)_2(\text{OH})_2$ . The percentage of copper is estimated



as in copper sulphate, the basicity as in ferric sulphate, the acetic acid by distillation with phosphoric acid, as in other acetates (see above).

**Ferrous Acetate, Acetate or Pyrolignite of Iron, Black Mordant.**—Mineral acid should be absent, but the preparation generally contains free acetic acid; it frequently contains ferric chloride, Glauber's salt, sodium chloride and tarry matter, and is adulterated with ferrous sulphate. *Pure* ferrous acetate is obtained by double decomposition from lead acetate and ferrous sulphate (used for chamois and hence known as "chamois mordant"). *Pyrolignite* of iron is prepared from ferrous sulphate and crude acetate (pyrolignite) of lime, thus it generally contains some sulphate. It also contains many tar products in solution, such as pyrocatechol, phenols, acetone, wood-spirit, etc., but it should contain nothing insoluble. This is a very important point. A mordant, which deposits tar constituents on standing in the air, especially matter of a soft, sticky and resinous nature, must be rejected, since its use would involve the risk of producing spotted pieces. The deposition of a light brittle crust is, on the other hand, often not to be avoided and is without danger. The strength of pyrolignite of iron varies greatly, and must accordingly be estimated, together with the sulphuric acid. The following are the results of analyses of three samples—

|      |     |           |                     |     |           |                    |
|------|-----|-----------|---------------------|-----|-----------|--------------------|
| I.   | 16  | per cent. | of ferrous acetate, | 7.8 | per cent. | of SO <sub>3</sub> |
| II.  | 4   | "         | "                   | "   | 5.0       | " "                |
| III. | 5.3 | "         | "                   | "   | traces    | " "                |

In case free acetic acid and, except sulphuric, no other acid is present, the acetate of iron may be estimated by difference.

*Total Iron.*—Since the tarry matters interfere with the estimation, an accurately weighed quantity is evaporated to dryness, the residue ignited and the iron determined in the ash gravimetrically or volumetrically (see *Ferric Sulphate*). *Sulphuric acid* is similarly estimated by evaporation of a weighed quantity, ignition of the residue with soda and saltpetre, solution in dilute hydrochloric acid and precipitation with barium chloride as barium sulphate.

In case no noteworthy quantity of alkali salts or of other metals except iron is present, the sulphuric acid is calculated as ferrous sulphate and the remainder of the iron taken as acetate.

*Acetic Acid.*—If noteworthy quantities of alkali salts are present (evaporation of the filtrate after precipitation of the iron by ammonia), such a method of calculation cannot be adopted. The acetic acid is then estimated by distillation with phosphoric acid and titration of the distillate (see *Acetates*).

*Practical Test.*—In addition to the chemical analysis a practical test must be made, since it is impossible to calculate the effect of the tarry matters. This test will naturally approach as nearly as possible to the large scale practice.

*Application.*—In silk-dyeing (blue-black), for dark shades of alizarine red; in cotton-dyeing more rarely on account of its high price. "Chamois mordant" (above) is used for pale chamois shades.

$$\begin{array}{c} \text{CO}_2\text{OH} \\ | \\ \text{Oxalic Acid (and Oxalates)}, \quad | \quad 2\text{H}_2\text{O} = 126, \text{ solu-} \\ | \\ \text{CO}_2\text{OH} \end{array}$$

bility = 1 : 9.

Oxalic acid and its salts often contain sulphuric acid; if this be absent, an acidimetric estimation is sufficient in the case of oxalic acid.

*Total Acid.*—50 grammes are dissolved to 1,000 c.c. and 50 c.c. titrated with N caustic soda and phenolphthalein: 1 c.c. of N soda = 0.063 gramme of crystallised oxalic acid. If sulphuric acid is present in quantity, the

*Oxalic acid* is estimated by oxidation with permanganate. To 20 c.c. of the above solution are added 25 c.c. of sulphuric acid (1:3) and the mixture titrated at 60 to 70 °C. by  $\frac{1}{5}$  N permanganate. 5 mols. of oxalic acid = 2 mols. of  $\text{KMnO}_4$ , or 1 c.c. of  $\frac{1}{5}$  N permanganate solution = 0.0126 gramme of  $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ .

A quantitative estimation of *sulphuric acid* is generally unnecessary; if required, the sulphuric acid is precipitated as barium sulphate, etc. Otherwise, the difference between total acid and oxalic acid gives the sulphuric acid.

It should be observed that oxalates are not included in an acidimetric estimation, but are titrated together with oxalic acid by permanganate; also sulphates are included in a gravimetric estimation of  $\text{SO}_3$ , but not determined by titration of the total acid.

In other respects oxalic acid must give a clear solution and contain little lime.

The amount of oxalic acid in the *oxalates* is estimated as above with permanganate, the metal according to the ordinary processes.

*Application.*—In dyeing wool with cochineal (formerly tin crystals were alone used), in printing on wool, instead of acetic acid (20 grammes of oxalic acid per 1 kilo. of colour); in mordanting wool with bichromate, etc. (in place of tartar); ammonium oxalate is used—similarly to ammonium acetate—in order to make the fibre absorb the dye (induline) more slowly and evenly; in calico-printing to remove iron and alumina; in washing to remove iron moulds; to remove Prussian blue from the fibre, as an addition to direct black.

*Chromium oxalate* in calico-printing

*Stannic oxalate* in printing alizarine colours.

*Stannous oxalate* as a reducing agent and discharge, especially for silk and half-silk goods.

*Ammonium oxalate* has been proposed as a substitute for tartar emetic, but has been little used (see *Tartar Emetic*).

**Tartaric Acid**,  $\text{C}_4\text{H}_2(\text{OH})_2(\text{CO}_2\text{OH})_2$  mol. wt. 150; readily soluble in water.

The ordinary impurities of tartaric acid are sulphuric acid, oxalic acid and lime (detected by barium chloride, calcium sulphate and ammonium oxalate respectively). The residue on ignition, the solubility, and the amount of acid may also be examined; the last-named is estimated by titration with standard soda or baryta water. 1 c.c. of N soda = 0.075 gramme of tartaric acid.

If the tartaric acid is very crude, and largely contaminated by other acids or deep in colour, it may be examined by the method II. given for tartar (below).

*Application.*—Tartaric acid, on account of its high price, is as little used as possible, but is still extensively employed,

In silk-dyeing for brightening; in calico-printing brighter shades are produced by tartaric acid (5 to 10 grammes per kilo. of colour); in wool-dyeing. It is, however, most largely employed in the form of tartar.

**Potassium Bitartrate, Tartar**,  $C_4H_2(OH)_2(CO_2O)_2$  ( $CO_2OK$ ) = mol. wt. 188.1; solubility, cold water = 0.4:100; hot water = 71:100.

It comes into the market in very varying degrees of purity: "crude," "half crystal," and "pure", according to the purity and colour one or the other method of examination must be used.

I. Crude tartar: 10 grammes of tartar are boiled with 7 grammes of potassium carbonate and 150 c.c. of water for twenty to thirty minutes in a 200 c.c. flask, the volume made up to the mark, the flask shaken, 100 c.c. filtered, evaporated to 25 c.c., 5 c.c. of acetic acid added, the mixture stirred, covered, and warmed for fifteen minutes on the water-bath. Then 100 c.c. of absolute alcohol are added, the liquid well stirred and allowed to stand for fifteen minutes. The separated pure tartar is filtered off with the pump, and washed with 96 per cent. alcohol, until the alcohol after dilution with water gives an alkaline reaction with one drop of N caustic soda. The tartar is then titrated by  $\frac{1}{2}$  N caustic soda, which has been standardised against tartaric acid or tartar, using sensitive litmus paper or phenolphthalein as indicator (see Fresenius, *Zeits. anal. Chem.*, xxii, 270).

II. Scheurer-Kestner's process is simpler (*Comptes rend.*, lxxxvi., 1024). The tartar is extracted with hydrochloric acid, the filtrate neutralised with caustic soda and the tartaric acid precipitated by means of calcium chloride as calcium tartrate. The precipitate is washed, dried and calcined; in the residue the calcium carbonate is determined volumetrically or gravimetrically and the result calculated to tartar. 1 mol. of potassium bitartrate = 1 mol. of  $CaCO_3$ .

III. If the tartrate is pure and free from foreign acids (or other substances combining with alkali) it can be titrated directly with N soda in a similar manner to tartaric acid. 2 to 3 grammes are taken. 1 c.c. of N soda = 188.1 milligramme of tartar. •

*Application*.—Principally in combination with potassium bichromate in mordanting wool, recently tartar has been subjected to an energetic competition by cheaper substitutes. Most of the substances offered as substitutes for tartar consist of oxalic acid, common salt, alum, Glauber's salt and similar substances. Herzinger has published the following recipe: 2 parts of common salt, 2 parts of tartaric acid and 5 parts of Glauber's salt are mixed and allowed to stand for some time, then 4 litres of water, 200 grammes of tin crystals and 400 grammes of sulphuric acid are added ("Tartar preparation" = sodium bisulphate, which see).

**Tartar Emetic, Antimony, Potassium Tartrate**,  $C_4H_4O_6K(SbO) \cdot \frac{1}{2}H_2O$  = mol. wt. 332.2; solubility, cold water = 7 : 100; hot water = 53 : 100. Contains 43.4 per cent. of antimony oxide.

The antimony and tartaric acid are determined. The principal impurity is oxalic acid, which is detected in the filtrate from the antimony, after driving off the sulphuretted hydrogen, by means of ammonia and calcium chloride or sulphate.

*Antimony*.—(a) 10 grammes of the substance are dissolved to 1,000 c.c. and in 50 c.c. (— 0.5 gramme of substance) the antimony is precipitated by sulphuretted hydrogen, brought on to a weighed filter paper (dried at 100° C.), the precipitate dried at 100° C., washed with carbon bisulphide, and weighed as  $Sb_2S_3$ .

(b) 50 c.c. of the above solution are mixed with 20 c.c. of a 10 per cent. sodium bicarbonate solution and 25 c.c. of a 2 per cent. bleaching powder solution and the mixture well stirred. If sufficient bleaching powder has been added, a drop of the solution gives a blue coloration with potassium iodide starch paper. It is now titrated with  $\frac{1}{10}$  N sodium arsenite solution, until a drop of the solution no longer gives a blue coloration when brought upon potassium iodide starch paper. A volume of bleaching powder solution, equal to that used above, is now titrated alone and the chlorine required to oxidise the antimony calculated to arsenite (W. B. Hart). 1 c.c. of  $\frac{1}{10}$  N sodium arsenite solution = 0.00651 gramme of Sb = 0.00721 gramme of  $Sb_2O_3$ .

Example: 0.5 gramme of tartar emetic, 25 c.c. of bleaching powder solution, and 7.5 c.c. of  $\frac{1}{16}$  N arsenite solution (25 c.c. of bleaching powder solution require 36.5 c.c. of arsenite);  $36.5 - 7.5 = 29$  c.c. of arsenite solution are used by the antimony, then

$$\frac{0.00721 \times 29 \times 100}{0.5} = 41.82 \text{ per cent. of } \text{Sb}_2\text{O}_3.$$

**Tartaric Acid.**—The filtrate from the antimony sulphide is boiled to drive off sulphuretted hydrogen, and the tartaric acid determined by one of the methods described under *Tartar*, e.g., method II. It should be stated that the percentage of antimony alone does not indicate the purity of the compound, since tartar emetic may be adulterated by other antimony salts, containing even more antimony than tartar emetic (antimony salt,  $\text{SbF}_3 \cdot (\text{NH}_4)_2\text{SO}_4$ , contains 47 per cent. of  $\text{Sb}_2\text{O}_3$ , double antimony fluoride,  $\text{SbF}_3 \cdot \text{NaF}$ , contains antimony equivalent to 66 per cent. of  $\text{Sb}_2\text{O}_3$ ).

**Application.**—As a mordant for cotton in combination with tannin, in fixing basic dyes, antimony potassium oxalate,  $\text{K}_2\text{Sb}(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$  (23.7 per cent. of  $\text{Sb}_2\text{O}_3$ ) has been introduced for the same purpose, but cannot replace tartar emetic in all cases. Another substitute is “antimony salt” or “tartar emetic substitute” (see above). Tartar emetic is also one of the materials from which the little-used aniline tartrate is prepared.

**Citric Acid**,  $\text{C}_6\text{H}_4(\text{OH})(\text{CO}_2\text{OH})_3 \cdot \text{H}_2\text{O}$  210, readily soluble in water.

Generally applied in the form of lemon juice, which occurs in commerce as a 25 per cent. syrup. Often adulterated by cheaper acids—oxalic, tartaric and sulphuric. Heavy metals may also be found. Oxalic acid is detected by means of lime water and ammonia, or calcium sulphate or chloride. Tartaric acid is detected by heating for one hour with strong sulphuric acid at 60 to 70°C.; if tartaric acid be present, a black or brown coloration is obtained. Citric acid may readily be detected in this manner. The citric acid, or lemon juice, is also titrated. 50 grammes are dissolved to

1,000 c.c. and 100 c.c. titrated with N caustic soda and phenolphthalein, 1' c.c. of N caustic soda = 0.07 gramme of crystallised acid - 0.06½ gramme of anhydrous citric acid.

*Application.*—As a consequence of the high price is little used. Principally in silk-dyeing for brightening (lemon juice); also as a discharge for alizarine colours; also, similarly to oxalic acid, to remove alumina and iron from the fibre; in finishing silk goods.

**Lactic Acid**,  $\text{CH}_3(\text{OH}) \cdot \text{CO} \cdot \text{OH}$  = mol. wt. 90. Miscible with water.

Quite recently lactic acid has been brought into the market, as a substitute for tartar, oxalic acid and tartar preparations, in the form of a 50 per cent. syrup. The strength is determined, as of the other organic acids, with N caustic soda and phenolphthalein. 1 c.c. of N soda = 0.09 gramme of lactic acid. The impurities are sulphuric, acetic and oxalic acids. If these are present in appreciable quantity quantitative estimations of each must be made under proper conditions. If oxalic acid be present, its percentage must be deducted.

*Lactic Acid.* 1 gramme of the acid is dissolved in 100 c.c. of water, 3 grammes of caustic potash (dissolved in a little water) added, and a 5 per cent. permanganate solution added, with continuous shaking, until the originally green solution becomes bluish-black, which colour must remain in the subsequent boiling. During boiling manganese peroxide is precipitated. After cooling, hydrogen peroxide is added until the solution is colourless, when the liquid is again boiled. The precipitate is filtered off, washed with hot water and the oxalic acid estimated in the filtrate by ordinary methods. The reaction is  $\text{C}_3\text{H}_6\text{O}_3 + 5\text{O} = \text{CO}_2 + \text{C}_2\text{H}_2\text{O}_4 + 2\text{H}_2\text{O}$  (Ulzer and Seidel, *Monatsh. für Chem.*, 1897, 135).

*Application.*—Principally as an assistant in mordanting wool with potassium bichromate; similarly with sulphuric acid and bichromate; the acid potassium salt (lactolin) is also recommended. Said to give better equalisation than tartar. Proposed for brightening silk. Put on the market as zinc, etc., salts by the firm of Bohringer.

## CYANOGEN COMPOUNDS.

**Sulphocyanides**,  $\text{CNS—M}$ , where M indicates a metal. The sulphocyanic acid may be estimated volumetrically in nitric acid solution with silver nitrate (the reverse of the silver or chlorine titration by Volhard's method). As in the titration of copper (which see), it is important to add the silver nitrate in excess, then acidify with nitric acid and titrate the excess of silver with  $\frac{1}{10}$  N ammonium sulphocyanide solution: 1 mol. of alkaline sulphocyanide = 1 mol. of  $\text{AgNO}_3$  or 1 c.c. of  $\frac{1}{10}$  N silver nitrate solution = 0.0097 gramme of  $\text{KCNS}$ .

*Neutral salts* may be titrated directly with silver solution, using potassium chromate as indicator.

*Application*—The sulphocyanides find very restricted employment in calico-printing, in dyeing they are not used.

*Aluminium sulphocyanide* for alizarine and as a resist for aniline black.

*Ten sulphocyanide* for alizarines.

*Chromium sulphocyanide*, instead of chromium acetate, for silk and half-silk goods.

*Potassium sulphocyanide*, on account of the ease with which it is decomposed, is used as a resist and discharge. It is printed with a suitable thickener.

*Barium sulphocyanide* has only been used experimentally.

*Cuprous sulphocyanide* is used in a very restricted manner for the sake of the copper it contains.

**Potassium Ferrocyanide, Yellow Prussiate of Potash, Sodium Ferrocyanide.**  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  = mol. wt. 422.2, solubility, cold water = 28, 100; hot water = 100, 100.  $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$  = 484, very soluble.

Potassium ferrocyanide and the less-used sodium salt may contain as impurities: potassium sulphate, carbonate and chloride, the potassium salt may contain the sodium salt. These impurities are detected in the solution immediately or after fusing in a porcelain crucible with potassium nitrate and extracting with water (Cl). The potassium or sodium ferrocyanide is directly estimated by the following processes:—



I. 20 grammes are dissolved in 1,000 c.c.; 20 c.c. of the solution, mixed with 250 c.c. of water and 20 c.c. of sulphuric acid (1:3), are titrated with  $\frac{1}{5}$  N permanganate, until the red coloration appears. 1 c.c. of  $\frac{1}{5}$  N permanganate = 0.01117 gramme of Fe = 0.0844 gramme of potassium ferrocyanide (Fe  $\times$  7.556 = potassium ferrocyanide). The permanganate solution may be standardised against iron or against pure potassium ferrocyanide (20 grammes in 1,000 c.c., 10 c.c. titrated). For example, if 50 c.c. of permanganate are required, then 1 c.c. of permanganate = 0.004 gramme of ferrocyanide = 2 per cent., each 0.5 c.c. of permanganate = 1 per cent. of ferrocyanide. The above degree of dilution must be maintained, in more concentrated solutions the end-point is not so sharp. Gintl (*Zett's. anal. Chem.*, vi., 446) adds a trace of ferric chloride as indicator and titrates until the blue coloration disappears (see also Fresenius, *Quant. Anal.*, I. 378).

II. In case potassium carbonate is absent, potassium ferrocyanide may be titrated by a standard zinc sulphate solution in an ammoniacal tartaric acid solution (reversed titration of zinc salts, see also Donath and Hattensauer, *Chem. Zeit.*, 1890, 323; *J. S. C. I.*, 1890, 554).

1 mol. of  $K_4Fe(CN)_6$  = 2 mols. of zinc salt = 2 atoms of zinc.

1 gramme of  $K_4Fe(CN)_6 \cdot 3H_2O$  = 0.3096 gramme of Zn.

The zinc is entirely precipitated when a drop of the solution begins to give a blue coloration with a mixture of ferric chloride and acetic acid. Accordingly, the potassium ferrocyanide solution must be run into the solution of the zinc salt, or at the commencement a little ferric chloride, which remains unprecipitated by the ferrocyanide, is added to the zinc solution (zinc sulphate is best).

**Application.** Principally for the preparation of Prussian blue upon cotton, wool and silk, especially for silk which is to be dyed black; also for aniline black (very restricted use).

**Potassium Ferricyanide, Red Prussiate of Potash,**  
 $K_3Fe(CN)_6$  = mol. wt. 658.3; solubility, cold water = 40:100;  
 hot water = 80:100.

The principal impurities are potassium sulphate and

ferrocyanide. The sulphate is estimated as in potassium ferrocyanide; the ferrocyanide may be determined by direct titration with permanganate, which may in this case conveniently be  $\frac{1}{25}$  N. The ferricyanide is estimated indirectly by titration with permanganate after reduction to ferrocyanide. The reduction is accomplished, according to Gintl (Mohr, *Titrimethoden*, 6 Aufl., 237), very easily by means of sodium amalgam, several lumps of which, the size of a pea, are brought into a neutral or alkaline solution. The reduction is complete in ten minutes, the solution is then titrated with  $\frac{1}{25}$  N permanganate, 1 c.c. of which = 0.01117 gramme of Fe = 0.1317 gramme of potassium ferricyanide.

•*Application* As an oxidising agent for steam aniline black; as a discharge for indigo, alizarine blue, ceruleum, etc. (MgO or water glass is then added as a diluent); it is occasionally used for logwood black to oxidise the colouring matter.

#### DERIVATIVES OF THE FATS.

**Soap.**—Soaps consist principally of the neutral sodium or potassium salts of the fatty acids and water, together with larger or smaller quantities of common salt, caustic and carbonated alkalis, unsaponified fat, glycerin, etc., as impurities. The smaller the quantity of these impurities the higher is the quality of the soap.

Soda soaps, which are "salted out" in the process of manufacture, are known as curd soaps, if they contain added water they are called "cut" soaps, and if they contain the constituents of the residual liquors of the manufacture, they are known as "filled" soaps, which thus contain larger quantities of glycerin, caustic soda, salt, etc.

Potash soaps cannot be "salted out," with common salt, because a transformation into soda soap and potassium chloride would occur, they therefore contain, similarly to the "filled" soaps, all the impurities contained in the residual lyes—glycerin, excess of caustic potash, etc. On account of their consistency they are known as soft soaps.

In addition to these pure soaps, reduced qualities also come into the market, to which quantities of various materials have been added, *e.g.*, water glass, chalk, starch, borax, kieselguhr, Glauber's salt, mineral oil, clay, barytes, etc. Such soaps are tabooed in the textile industries; they are chiefly used for toilet or domestic purposes. The impurities are most readily detected by dissolving the soap in absolute alcohol, or in the ash. Pure soaps alone will be considered here.

The composition of soaps varies greatly; for each special purpose special properties are required. Calvert gives the following as the compositions of normal soaps for various consumers

|                                       | Fatty Acid<br>per cent. | Soda<br>per cent. | Water<br>per cent. |
|---------------------------------------|-------------------------|-------------------|--------------------|
| Normal soap for Calico printers . . . | 64.0                    | 6.0               | 30                 |
| " " " Cotton dyers . . .              | 66.0                    | 7.0               | 27                 |
| " " " Silk dyers . . .                | 61.9                    | 8.1               | 30                 |
| " " " Woollen manufacture . . .       | 61.4                    | 8.6               | 30                 |
| Best soap for madder violet . . .     | 60.4                    | 5.6               | 34                 |

The cause of the varying composition of soaps is to be found in the use in their manufacture of the most varied oils and fats, which have the power of combining different amounts of alkali and water. There are used: olive oil from various sources, the fatty acids of olive oil, palm oil, coconut oil, tallow, hemp-seed, rape seed and linseed oils, etc. Assuming that a soap contains no artificial additions, the following are the most important characters: the proportion of fatty acids, total alkali, free alkali and unsaponified fat. Of the greatest importance are also the nature and quality of the fatty acids; the proportion of common salt is less important. The percentage of water, which may be obtained by difference, may also conveniently be directly determined.

The most speedy and accurate method of conducting a soap analysis is commenced by making a stock solution, in which as many constituents as possible are estimated.

*Analysis.*—20 to 25 grammes of soap, cut from the interior of the piece, are dissolved to 1,000 c.c.

*Water.*—50 c.c. of the solution are placed in a porcelain dish containing about 10 grammes of ignited quartz sand, which has been weighed with the dish. The contents are evaporated to dryness on the water-bath and dried at 100° C., with the addition of a little alcohol, to constant weight. The addition of alcohol (a few c.c.) considerably facilitates the evaporation of the last portions of water. The loss in weight is water. This method is more rapid and accurate than the usual process of drying soap shavings first at 50° to 70° C. and then at 100° C. The latter process generally gives too little water, which remains enclosed in the interior of the soap.

*Fatty Acids.*—(a) 100 c.c. of the solution are decomposed with 20 c.c. of normal sulphuric acid in a thin-walled beaker, which has been weighed together with a glass rod. The mixture is heated on the water-bath until the fatty acids have separated as a clear layer and the lower aqueous solution has become almost completely transparent. The hot liquid is then filtered through a good Swedish filter paper (previously dried at 100° C. and weighed), and the oily layer washed with hot water until the filtrate no longer shows an acid reaction to sensitive neutral litmus paper. 200 c.c. of hot distilled water are, as a rule, sufficient. The filtrate is retained for the estimation of total alkali.

The filter paper containing the fatty acids is then placed in the weighed beaker used for the decomposition, the funnel washed with a few drops of petroleum ether if it shows traces of fat, and the beaker and its contents dried at 100° C. to constant weight. The increase in weight gives the fatty acid, which is converted into the corresponding amount of fatty acid anhydride by deducting 3.25 per cent. The filtrate must be completely clear and free from every trace or globule of fat; an opposite condition may be ascribed to the use of an unsuitable paper, to incomplete moistening of the paper before filtering, and to the "creeping" of melted acids along the folds of the paper and so over the edge.

Instead of a weighed filter, Gawalovsky (*Zeits. anal. Chem.*, xxlv., 219; *J. S. C. I.*, 1885, 369) prefers an ordinary unweighed paper, and washes the fatty acids, after they have solidified, with petroleum ether into the beaker. If the acids or the paper are wet, they are first moistened with a few c.c. of alcohol, which removes the water; the acids are then washed through with petroleum ether. The filter paper must be washed with petroleum ether until there is no trace of fat in the filtrate, *i.e.*, until about ten drops leave no residue on evaporation on a watch glass. Gawalovsky states that, when the fatty acids are dried together with the paper, capillary decompositions occur, which, however, according to the author's experience, hardly exceed 0.05 to 0.1 per cent. with careful working. On the other hand the process in which the acids are dried together with the paper, is far simpler and more rapid.

(b) Wax method. Instead of filtering off the fatty acids separated by sulphuric acid, they may be melted to a cake with about 10 grammes of pure wax (dry and not capable of giving up anything to water). The beaker is then rapidly cooled in ice or cold water, so that the cake of wax may separate completely from the glass. The cake is washed with cold water, freed from adhering drops of water by means of filter paper and dried in an exsiccator over sulphuric acid. The operation must be so conducted that the cake of wax (or paraffin) separates entirely, without leaving traces of wax or fat on the glass; with some practice this is easy. If the separation is not successfully accomplished, the beaker may be dried and weighed, and the increase in weight added to the weight of the cake. This method generally gives appreciably higher results than the preceding, since more or less water always remains enclosed in the interior of the cake and cannot be removed even by very long drying in the exsiccator.

*Total Alkali.*—(a) The filtrate from the fatty acids (a) or the solution obtained after removing and washing the wax cake (b) is titrated back with normal caustic soda and phenolphthalein. The volume of soda solution used, deducted from the 20 c.c. of normal acid originally added, corresponds to

100 c.c. of the soap solution. 1 c.c. of normal sulphuric acid = 0.031 gramme of  $\text{Na}_2\text{O}$ .

(b) 100 c.c. of the soap solution may also be directly titrated with normal acid and methyl orange until the pink coloration appears. The results agree very well with those obtained by process (a). 1 c.c. of normal acid = 0.031 gramme of  $\text{Na}_2\text{O}$ .

*Sodium Chloride.*—The solution used for the estimation of the total alkali may now serve for the determination of sodium chloride. In case the solution is coloured pink, it is decolourised by 1 drop of  $\frac{1}{10}$  N sulphuric acid or by means of the carbonic acid in the breath, a few drops of a neutral solution of potassium chromate are added and the liquid then titrated with  $\frac{1}{10}$  N silver nitrate solution until the brown coloration begins to appear. 1 c.c. of  $\frac{1}{10}$  N silver nitrate solution = 0.00584 gramme of  $\text{NaCl}$ . Good curd soap generally contains 0.4 to 0.8 per cent. of  $\text{NaCl}$ .

*Free Alkali.*—The estimation of the free alkali is a delicate process, since only hundredths of a per cent. have frequently to be determined and only 0.1 per cent. is often quite impermissible. An approximate idea of the alkalinity of a soap may be obtained by moistening a freshly cut surface with mercuric chloride solution—a brownish-yellow to reddish-brown coloration appears according to the amount of free alkali. The degree of alkalinity may also be roughly ascertained by the taste—by laying a freshly cut surface on the tongue.

Of the many chemical methods for the quantitative estimation of free caustic soda, the following is to be regarded as the most reliable and speedy.---

(a) 500 c.c. of the solution (10 to 12 grammes of soap) are heated with 200 grammes of common salt (neutral, or of known alkalinity, which is deducted in the calculation) in a flask, provided with a Bunsen valve, on the water-bath, until all the salt has dissolved, the soap has separated in curdy masses and the aqueous solution has become clear. The flask is then cooled, the contents filtered through a large folded filter into a 1 litre flask, the filter washed with a saturated solution of common salt, and the filtrate made up

to 1 litre. Then 500 c.c. are brought into a beaker, excess of barium chloride solution is added, by which the carbonate is precipitated (see *Soda and Caustic Soda*), and the liquid titrated, without filtering, with  $\frac{1}{10}$  N hydrochloric acid and methyl orange (not phenolphthalein) until the red coloration begins to appear. 1 c.c. of  $\frac{1}{10}$  N hydrochloric acid = 0.0031 gramme of  $\text{Na}_2\text{O}$  as caustic soda. The second 500 c.c. are titrated with  $\frac{1}{10}$  N hydrochloric acid and methyl orange, without the addition of barium chloride. 1 c.c. of  $\frac{1}{10}$  N hydrochloric acid = 0.0031 gramme of  $\text{Na}_2\text{O}$  as soda + caustic soda. The difference between the two titrations gives the sodium carbonate.

In view of the small quantity of caustic soda which is generally to be determined, a correction of the following kind must inevitably be made: 200 grammes of common salt of the same quality are dissolved under exactly the same conditions, the solution filtered, brought to 1,000 c.c., and two quantities of 500 c.c. each titrated, with and without barium chloride, with  $\frac{1}{10}$  N hydrochloric acid and methyl orange. The volumes of acid required in these experiments until the commencement of the red coloration (orange coloration) are deducted from the volumes used in the soap titrations. This consumption of acid, until the end-reaction occurs, is not to be ascribed alone to the alkalinity of the common salt; it would be necessary with perfectly neutral salt, since the sensitiveness of indicators in such dilute solutions and in strong salt solutions is less than in stronger solutions containing less salt. On the other hand a certain degree of dilution is necessary, since in strong solutions of soaps, the latter, on precipitation, enclose a certain amount of alkali, which would thus be lost. The use of phenolphthalein at these dilutions and in presence of so much common salt must be regarded as quite excluded and unreliable.

In the case of an almost neutral soap a quantity of 10 to 12 grammes is not sufficient, it is necessary to take a larger portion. Frequently 30 to 50 grammes of soap are dissolved in 600 c.c. of water, the soap precipitated as above with 200 grammes of salt, the liquid cooled, filtered into a 500 c.c.

flask, and two quantities of 250 c.c. taken, etc. Exactly as described above, one half is titrated with  $\frac{1}{10}$  N acid with, the other half without, barium chloride.

(b) 7 to 8 grammes of soap are dissolved to a very strong solution in 40 to 50 c.c. of water, salted out with common salt, the mixture filtered, the filtrate evaporated, the residue extracted with absolute alcohol, when alkaline carbonate remains undissolved, the solution diluted with water and titrated with  $\frac{1}{10}$  N hydrochloric acid. This method, which is still much used, is to be regarded as quite untrustworthy since (1) caustic soda in appreciable quantity remains enclosed in soap separated from a strong solution; (2) during the evaporation of the solution the caustic soda has too much opportunity for absorbing carbonic acid from the air, and (3) the alcohol considerably diminishes the delicacy of the end-reaction.

(c) About 30 grammes of soap are dissolved in alcohol free from acid and the solution filtered, the filtrate is titrated with  $\frac{1}{10}$  N hydrochloric acid and phenolphthalein. This method, also, is inaccurate, since (1) phenolphthalein is not sensitive in alcoholic solution; (2) phenolphthalein also always absorbs some alkali. Most *alcoholic* solutions of soaps do not give alkaline reactions with phenolphthalein even when they contain 0.1 per cent. of free soda (see also C. and N. Draper, *Chem. News*, iv., 133; *Zeits. anal. Chem.*, 1886, 51; Gawalovsky, *Zeits. anal. Chem.*, 1888, 155; *J. S. C. I.*, 1885, 169; Hope, *Chem. News*, xlv., 219).

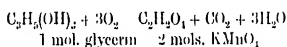
(d) The process of Möllit is quite inaccurate and inconvenient: 10 grammes of soap are dissolved in 150 to 180 c.c. of alcohol, the solution is filtered and the residue washed with alcohol in a hot-water funnel. A current of well-washed carbon dioxide is passed over the surface of the liquid, when the alkali is precipitated as carbonate, which is filtered off, washed with alcohol, dissolved in water and titrated in the usual manner (see also W. Walke, *Chem. Zeit.*, 1896, 16, 137).

*Alkaline carbonate* is frequently not estimated, since, even in cases where the absence of caustic alkali is rigidly demanded, it is of little importance, as it can only ad-



vantageously neutralise the hardness of most waters. A considerable excess of soda would naturally be very harmful; the methods of soap-making, however, would almost always cause the excess of sodium carbonate to be in a certain proportion to the free caustic alkali. The soda may be determined as already described under *free alkali*; the filtrate from the salted-out cake of soap is titrated with  $\frac{1}{10}$  N hydrochloric acid and methyl orange, with and without barium chloride. Each 1 c.c. of  $\frac{1}{10}$  N acid of the difference = 0.0031 gramme of  $\text{Na}_2\text{O}$  as sodium carbonate. The harmfulness of the soda is, as already indicated, dependent upon the hardness of (proportion of lime in) the water. (For the estimation of sodium carbonate, silicate and borate in soap, see W. Waltke & Co., *Chem. Zeit.*, 1896, No. 3, p. 20.)

*Glycerin* may be estimated in the liquids which have been used for the determination of sodium chloride, total alkali or caustic alkali. The whole, or an aliquot portion, is evaporated to dryness, the residue extracted with absolute alcohol at  $80^\circ$  C., and the solution evaporated. When the glycerin obtained is impure, it can be titrated by Benedikt and Zsigmondy's method with permanganate in alkaline solution (see Benedikt or Lewkowitsch, *Analysis of Oils*, etc.).



Or, and this is preferable, if the quantity of glycerin be small, a larger quantity of soap is taken (20 to 25 grammes), dissolved in water, sulphuric acid added to acid reaction, the fatty acids removed by one of the above methods—with wax or by filtering, the filtrate neutralised with potassium carbonate, evaporated to dryness, the residue ground in a mortar and extracted with absolute alcohol. The mixture is filtered into a tared beaker, and heated to constant weight on the water-bath, or better at  $50^\circ$  to  $60^\circ$  C. The residue is glycerin, the result may be checked by titrating with permanganate as above.

*Unsaponified Fat.* - About 25 to 30 grammes of very finely powdered soap (when the water is estimated, the dry soap

powder may be weighed; otherwise the, moist soap must first be dried) are extracted in a Soxhlet's extractor for three to four hours with petroleum ether. The ether is evaporated and the fat weighed. Since soap is also soluble in petroleum ether to a slight extent, the ethereal solution must be poured off from any soap which has separated in the flask, the latter washed out and a correction made for the solubility of soap in petroleum ether. 100 c.c. of petroleum ether dissolve 0.01 gramme of Marseilles soap.

*Melting and Solidifying Points of the Fatty Acids.*—Endeavours to recognise the nature of the fatty acids are generally restricted to determinations of their melting and solidifying points. More rarely the specific gravity, iodine value, etc., are taken (see Benedikt, *Analyse der Fette und Wacharten*, Abschnitt x., xi.; Lewkowitsch, *Analysis of Oils, Fats and Waxes*, fifth ed., vol. in., pp. 313-354).

The fatty acids, separated by dilute sulphuric acid from a strong boiling solution of the soap (100-800) contained in a beaker, are allowed to cool and kept in the cold for at least twenty-four hours. The odour evolved during the decomposition of the soap should be observed, important conclusions may thus sometimes be drawn. After removing and drying the fatty acids in the exsiccator, the melting and solidifying points are taken. In the case of a homogeneous product these temperatures should lie near together.

(a) Bach (*Chem. Zeit.*, vii., 356) fills the acids into a narrow thin-walled test-tube, allows them to solidify and then warms the tube in a beaker of water heated with a small flame. The mass is stirred gently with a thermometer and the point noted at which the whole becomes completely clear. This is the melting point. The temperature, at which flocks begin to collect round the thermometer on cooling, is the solidifying point.

(b) Benzenmann (*Repert. der anal. Chem.*, iv., 165) determines the beginning and ending of the fusion in the following manner: A piece of glass tube is drawn out so that the narrower and wider portions are equal in length, the narrow end is then fused up; two to three drops of the fat are brought into the tube immediately above the constriction

and allowed to solidify (solidification effected by one drop of ether). The tube is then placed in an upright or slightly inclined position in a beaker filled with cold water, in which a thermometer is hung. The beaker is heated as slowly as possible, by means of a small flame, until the drop of fatty acids just begins to run down. The temperature observed at this moment is "the commencement of fusion". The temperature, at which the turbid drop, on further heating, becomes quite transparent, is "the end of fusion".

The melting point is determined by many different methods, which give varying results. There is the uncertainty whether the temperature at which the fat begins to be fluid, or that at which it becomes clear, is to be designated the melting point. In general the former is taken, *i.e.*, the temperature described by Bensemann as "the commencement of fusion".

(c) Other methods give as the melting point that temperature at which, *e.g.*, the fat when placed in a narrow tube, open at both ends and heated in water, begins to rise in the tube.

(d) According to another method hollow glass spheres are placed in a wide test-tube filled with the fatty acids, which are continuously stirred with a narrow thermometer. The melting point is the temperature at which the spheres begin to rise.

(e) Similarly the solidifying point is the temperature at which the hollow spheres, when pressed down by means of the thermometer, do not rise again. For this operation cooling with water is generally sufficient; the temperature of the water should be several degrees below the melting point.

*Molecular Weight of the Fatty Acids.* Frequently the molecular weight (or the saponification value) of the fatty acids indicates the nature of the fat or oil employed: 5 grammes of completely dry fatty acids are dissolved in 60 to 70 c.c. of hot neutral alcohol and titrated with normal alcoholic potash and phenolphthalein. The weight of fatty acid taken, multiplied by 1,000 and divided by the number of c.c. of normal potash used, gives the molecular weight.

Thus 5 grammes of fatty acid required 18 c.c. of N caustic potash:  $\frac{5 \times 1000}{18} = 277.7$ , the molecular weight required, assuming the acid to be monobasic.

*Resin.*—(a) If the soap is free from potash salts and unsaponified fat, the dry soap may, according to Barfoed, be extracted directly with ether-alcohol, in which sodium salts of the fatty acids are insoluble.

(b) If the soap contains potash salts the resin is estimated in the separated fatty acids, together with which it is precipitated (Barfoed, *Zeits. anal. Chem.*, xiv., 29). The fatty acids are neutralised with normal (or stronger) caustic soda, dried at 100° C. to constant weight, and heated with absolute alcohol (10 c.c. to 1 gramme of substance) to 80° C., when the resin and a portion of the fatty acid soap dissolve. After cooling, evaporated alcohol is replaced and 5 volumes of pure ether added, when the fatty acid soap is completely precipitated. Ether is then added to bring up to a definite volume, the mixture shaken from time to time for several hours, allowed to stand twenty-four to forty-eight hours, an aliquot part of the clear liquid withdrawn, brought into a weighed dish and evaporated to constant weight at 100° C.

(c) 2 to 3 grammes of the mixture of resin and fatty acids are dissolved in 25 to 30 c.c. of absolute alcohol in a small flask, and dry hydrochloric acid gas passed in, whilst cooling. The fatty acids are then converted into ethyl esters, whilst the resin acids remain unaltered. When no more gas is absorbed and the esters have separated (in about forty-five minutes) the flask is allowed to stand thirty minutes longer; 100 to 125 c.c. of hot water are then added, and the mixture shaken with 50 to 75 c.c. of petroleum ether in the separating funnel. The resin is dissolved by the petroleum ether, the solution is first washed with water and then shaken with a solution of 0.5 gramme of caustic potash in 5 c.c. of alcohol and 50 c.c. of water, when the resin acids separate, they are weighed on a tared filter (J. Landin, *Chem. Zeit.*, 1897, 25).

*Inorganic and organic added matter* may be detected in the ash and aqueous or alcoholic soap solutions, respectively. The principal substances used for this purpose have already been mentioned.

*Applications.*—On the widest scale for all textile fibres. In silk-dyeing for scouring, soaping and dyeing, especially in black silk dyeing (neutral); in calico-printing; in wool-washing together with ammonia; in dyeing wool with alkali blue; in fulling woollen goods (free caustic soda and fat must be absent); for brightening (free alkali may be harmful). On a large scale in the cotton industry, to remove grease, etc.

"**Boiled-off Liquor**" is obtained in silk-dyeing. Its quality depends upon the strength of the soap employed and the nature of the silk fibre. In the absence of "boiled-off liquor" Sartori recommends the following:

1. 400 grammes of Marseilles soap are dissolved in 15 litres of boiling water and a solution of 100 grammes of size added. Finally 0.05 litre of olive oil is introduced in small quantities. The solution should be used cold (*Färberei-Muster-Zeit.*, 1888, 333).

2. Another recipe is: 25 grammes of Marseilles soap and 4 to 6 grammes of gelatine are dissolved in 1 litre of water.

3. Or 20 grammes of Marseilles soap with 2 grammes of gelatine and 1 gramme of common salt are dissolved in 1 litre of water.

*Application.*—In silk-dyeing, generally in a bath acidified with sulphuric or acetic acid (for eosine). Glauber's salt (which see) is also often added.

**Turkey Red Oil.** Widely different substances are sold under the names of "Turkey red oil" or "red oil," they vary according to the nature of the oil employed and the method of treatment. Amongst others the following are used: castor, olive, tournant, cotton-seed, rape-seed and coconut oils, oleic acid, and mixtures of these. The most valuable Turkey red oil is obtained from castor oil.

Opinions vary as to the nature of the reaction (see Benedikt, p. 147 *et seq.*; Lewkowitsch, fifth ed., vol. i., p. 215, vol. iii., p. 195). The greater portion of Turkey red oil consists of ricinoleic acid; the smaller—but more valuable—part of ricinoleo-sulphuric acid and hydroxyoleic acids. The Badische Anilin- und Sodafabrik accordingly bring two qualities into the market: Turkey red oil D = sodium

ricinoleate, and Turkey red oil F = sodium (or ammonium) ricinoleo-sulphate. The method of preparation consists in acting upon the above-mentioned oils with fuming sulphuric acid and then neutralising with soda or ammonia.

Turkey red oil is analysed in a similar manner to soaps. Preliminary examination: The oil must be slightly alkaline or neutral; it must yield a complete emulsion with water, from which drops of oil separate only on long standing. These drops of oil must give a clear solution with ammonia, if they do not give a clear solution they contain unsaponified fat.

*Water.*—According to Stein, 10 grammes of the oil are melted together with 25 grammes of dry wax in about 75 c.c. of a saturated solution of common salt. The cake is dried and weighed. The increase in weight of the wax represents anhydrous oil; the difference between this and the weight taken gives the water.

*Total Fat* (Bruhl, *Zeits. anal. Chem.*, xvi., 448, and Stein, *Ber.*, xii., 1174).—4 grammes of the sample are weighed into a thin-walled hemispherical glass dish, which was previously weighed together with a glass rod, 20 c.c. of water are then gradually added with continuous stirring. If the liquid is turbid, ammonia is added until the reaction is slightly alkaline towards phenolphthalein, 15 c.c. of sulphuric acid (1 : 1) are then added, next 6 to 8 grammes of stearic acid. The liquid is then gently boiled, until the fat separates clear, when it is allowed to cool, the solidified cake removed together with the glass rod and placed on filter paper. The residual liquid is again heated in the dish until the particles of fat have united to 1 or 2 drops. The dish is removed from the water-bath, and inclined so that the drops of fat adhere to the side. The liquid is poured off, the dish washed out with water and the cake returned to it. The dish is then heated on a sand-bath with continuous and uninterrupted stirring by means of the glass rod, until the crackling sound is no longer heard and white vapours begin to be evolved. The dish is then allowed to cool, weighed, and the weight of dish, glass rod and stearic acid deducted. The remainder gives the total fat.

*Neutral Fat.*—About 30 grammes of the sample are dissolved in 50 c.c. of water, 20 c.c. of ammonia and 30 c.c. of glycerin added and the mixture twice extracted with 100 c.c. of ether. The ether is shaken with water in order to remove traces of soap, the solvent distilled off, the residue brought into a tared glass dish, dried first on the water-bath, then in the air-bath, and weighed.

*Soluble Sulphated Fatty Acids* (sulphuric esters of the fats).—The value of Turkey red oil depends principally on the proportion of ricinoleo-sulphuric acid: 5 to 10 grammes of the sample are dissolved in 25 c.c. of water in a thick glass flask, 25 c.c. of fuming hydrochloric acid added and the mixture heated for one hour in the oil-bath at 130° to 150° C. After diluting and transferring to a beaker, the layer of oil is filtered off. This is most easily accomplished if an unweighed quantity of stearic acid be added, the liquid boiled and allowed to cool. In the filtrate the sulphuric acid is precipitated by barium chloride, the sulphuric acid present as sulphate (see below) deducted, and the remainder calculated into ricinoleo-sulphuric acid by multiplication by the factor 4.725.

*Fatty acids* may be present either free or combined with soda or ammonia. The amount is found by deducting the neutral fat and sulphated acids from the total fat (see above). The difference corresponds to the fatty acids, which, after deduction of 3.15 per cent., may be inserted as acid anhydrides in the result of the analysis.

*Sulphuric Acid.* In order to estimate the sulphuric acid present as alkaline sulphates, the solution of the oil in ether is several times shaken with a few c.c. of a saturated solution of pure sodium chloride. The extracts are united, diluted, filtered and precipitated with barium chloride. The total sulphuric acid contained in the oil may also be estimated by fusing with caustic potash and saltpetre, and the proportion of sulphated acids or sulphates calculated by difference.

*Ammonium and Sodium.*—7 to 10 grammes of oil are dissolved in ether and shaken four times with quantities of 5 c.c. of dilute (1 : 6) sulphuric acid. The united acid extracts are

evaporated on the water-bath for the estimation of soda, freed from excess of sulphuric acid by heating on the sand-bath and the residue finally converted by ignition into sodium sulphate, which is weighed (142 parts of  $\text{Na}_2\text{SO}_4$  = 62 parts of  $\text{Na}_2\text{O}$ ). In order to estimate ammonia, the oil is similarly extracted with dilute sulphuric acid, the extracts distilled with excess of caustic potash and the ammonia absorbed in a measured volume of standard sulphuric acid, the excess of which is titrated at the end of the operation (see also *Ammonium Salts*).

*Nature of the Oil.*—The acetyl and iodine values are taken of the total fat separated without the addition of stearic acid (see Benedikt). If pure castor oil had been used in the manufacture of the Turkey red oil, the former value is 110 or higher, the latter 70 or rather lower. If one or both of these values are found much smaller, the Turkey red oil has been made from a mixture of castor oil with another oil or from another oil alone, it is then to be regarded as of little value (olive oil, cotton seed oil, oleic acid, etc., see above and Benedikt).

*Practical Test.* The suitability of the oil should be examined by means of a practical test.

*Application.* In dyeing and printing Turkey reds. In finishing silk, silk mixture and cotton goods.

### TANNINS.

There is a large number of materials containing tannin (tannic acid, digallic acid) which are principally used on account of that constituent, and are evaluated accordingly: gall-nuts (30 to 40 per cent.); *Knoppern* (see p. 114), mirabolans, divi-divi (30 per cent.), catechu (brown and yellow, about 30 per cent.); sumac or sumach (10 to 18 per cent.); oak bark (6 to 10 per cent.); fir bark (8 to 10 per cent.), and the tannins obtained from these sources (up to 100 per cent.). Tannin is often adulterated by magnesium sulphate. *Prepared catechu* contains additions of alum and potassium bichromate, ammonium, etc.

Each of the above tannins has its own peculiar properties, the tannins or tannic acids from various sources are in no way



identical; thus the tannic acid of gall-nuts is a totally different substance from the tannic acid of catechu, etc.

H. R. Procter divides the known tannic acids into 3 groups according to the qualitative reactions they give (*J. S. C. I.*, 1894, 487). Two reagents are utilised: a 1 per cent. solution of iron ammonium alum (A), and bromine water (B).

Group I. Tannins which are precipitated by B and give a greenish-black coloration with A—catechu tannins.

Group II. Tannins which are precipitated by B and give bluish to violet-black colorations with A—mixtures or tannins of undefined character.

Group III. Tannins which are not precipitated by B and give a blue coloration with A—derivatives of pyrogallie acid.

*Distinctive Reactions.*—Tannin solution + copper sulphate solution + ammonia: a precipitate is always produced, which may dissolve in excess of the precipitant. If it remains undissolved, the tannin belongs to the group of the gall-nut tannic acids, or it contains protocatechuic acid.

Dilute tannin solution + 2 or 3 crystals of sodidm nitrite + 3 or 4 drops of very dilute sulphuric acid: a red coloration is generally produced, which slowly turns to purple and dark blue or to green and olive. Frequently a yellow or brown coloration or precipitate is at once produced; then a tannin producing ellagic acid is present (ellagic acid itself and gall-nut tannic acid do not give the reaction).

The tannins of the conifera, mimosa and certain other plants give with a strong hydrochloric acid solution of stannous chloride, 10 c.c. to 1 c.c. of tannin decoction, a pale red precipitate, which appears after about ten minutes.

When a tannin decoction is poured on pine splinters, which are moistened before and after drying with strong hydrochloric acid, a pale red or violet coloration is produced, catechu-tannic acid and phloroglucinol are indicated.

A few drops of a decoction of *Knopperrn* (galls formed on the acorn cups of a Hungarian species of oak), mixed in a dish with sodium sulphite crystals, give a purple-red coloration.

*Qualitative Examination.*—Tannin must give as clear a

solution in water as possible, and also in ether-alcohol (1 : 1). In the latter solvent there remain undissolved starch, milk sugar, dextrin, sugar, extractive matters, magnesium and sodium sulphates. Tannin is frequently adulterated with dextrin. A good tannin should contain about 90 per cent. of tannic acid and 7 to 8 per cent. of water. The ash should be low (see also F. Günther, *Ber. d. d. Pharm. Ges.*, 1895, v., 297).

*Quantitative Estimation of Tannic Acid.*—The proportion of tannic acid, which, as already stated, is extremely variable, determines the value, except in certain cases in which the presence of colouring matter is of importance. Many methods have been proposed for its estimation (see also Fresenius, *Quant. Anal.*, II. 484), which may be divided, according to the principle of the process, into the following :

I. Hydrometric methods, II. Titration with permanganate, III. Gravimetric hide-powder methods. The last is continually gaining ground over the first two, and when exactly considered is the most thorough, since it determines directly how much tannin (*i.e.*, a substance forming leathery matter with hide-powder) is present. The permanganate method is less reliable, since in this case the nature of the individual tannic acid comes into play and causes abnormalities.

I. The hydrometric methods are said to give favourable results. However, for each separate source of tannic acid a distinct table is necessary, so that in the case of abnormal impurities, adulterations, and unknown tannins the method cannot be used and is thus unsuitable for general purposes. For details of the hydrometric method see *Praktische Anleitung für Gerber zur Untersuchung der Gerbmaterialeien*, by Professor v. Schroder of Thara, 4 (to be obtained from the author, price 2 marks).

II. The permanganate method comprises two operations : (a) the titration of the total oxidisable matter ; (b) titration of the solution freed from tannic acid. The difference,  $a - b$ , gives the tannic acid.

(a) A quantity of the solution containing about 0.1 gramm of dry substance is titrated with  $\frac{1}{25}$  N permanganate, using indigo-sulphuric acid as indicator (25 c.c. of

a 0.1 per cent. solution of indigotin in sulphuric acid), until the liquid has acquired a yellow coloration. The consumption of permanganate by the 25 c.c. of indigo solution, determined by a separate experiment, is deducted.

(b) A second portion of the tannin solution is precipitated with gelatine or hide-powder and an aliquot part of the filtrate (see III.) titrated with permanganate and indigo solution as in b. The difference between *a* and *b* gives the tannic acid. The values obtained by titration (number of c.c. of permanganate) are generally not calculated to tannic acid, but to the equivalent quantity of oxalic acid. According to Neubauer and Oser, however, 0.063 gramme of oxalic acid corresponds to 0.04159 gramme of gallotannic acid (tannin) or to 0.06235 gramme of bark-tannic acid. Accordingly

$$\text{Oxalic acid} \times 0.666 = \text{tannin.}$$

$$\text{Oxalic acid} \times 0.99 = \text{bark-tannic acid.}$$

It will be noticed that the equivalents of the various tannic acids are so different that great errors might be the result of applying the method to a mixture of various tannic acids. The process is thus unreliable.

III. The gravimetric hide-powder method is to be regarded as giving the only *absolute* estimation. It comprises the following two single determinations: (a) Anhydrous extracted matters soluble in water, and (b) Extracted matters *minus* tannins, or "non-tannins".

(a) About 10 grammes, or a quantity corresponding to 10 grammes, of the tanning material is dissolved to 1,000 c.c., and 100 c.c. of the liquid, filtered through glass-wool, asbestos, etc. (not through paper, which absorbs tannin), is evaporated and dried at 100° C., to constant weight. The result is the "total extract".

(b) A further portion of the filtrate (containing 0.6 to 1.0 gramme of solid matter) is mixed with 10 grammes of the purest hide-powder, added gradually, until tannic acid can no longer be detected in the solution. The mixture is well stirred and when all the tannic acid is absorbed, 50 c.c. are filtered (paper may now be used), evaporated and dried at 100° C. The result gives the "non-tannins".

$a - b =$  tannin, which is calculated to 100 parts by weight. The method is very exact, easily and rapidly carried out and is scientifically unassailable. The purity of the hide-powder is naturally of importance, it ought not to contain any matter soluble in water, for which allowance would otherwise have to be made.

Procter conducts the analysis in the following manner: To 100 c.c. of a tannin solution, containing not more than 0.6 gramme of solids, are added, with intervals of stirring for ten minutes, three quantities of 2 grammes each of well washed and dried hide-powder. The mixture is thoroughly agitated by means of a stirring apparatus working at 320 to 420 revolutions per minute. After thirty minutes the whole of the tannin is absorbed, the liquid is then filtered and 50 c.c. of the filtrate evaporated to dryness. If the result be deducted from the weight of the total extract contained in an equal volume of the decoction, the difference gives the weight of tannin absorbed by the hide-powder. Since Procter does not use quite dry hide-powder, he notes the difference between the originally dry and the washed and pressed hide-powder, by weighing before and after, and allows 1 c.c. of water for each increase in weight of 1 gramme, which in the calculation must be added as a correction to the 100 c.c. of tannin solution. The use of an inconvenient hide-powder filter (see *Der Gerber*, 1887, 137) is not attended by essential advantages and hinders working.

If a complete analysis is required, water, insoluble matter, ash, etc., are determined.

IV. *Technical Examination.* Tannin analyses should be supplemented by comparative dyeing or weighing trials, which are carried out in a manner dependent on the particular tannin and its proposed use.

In this case, as always, the technical examination must be made as nearly as possible under actual working conditions. For example, 2 grammes of the sample (sumac, mirabolans) are boiled for fifteen minutes with 500 c.c. of water, and the whole decoction, including insoluble matter, made up to 500 c.c. To each beaker are then added 10 grammes of common salt, and at 90° to 95° C. 10 grammes of cotton yarn

are suspended in the liquid. After stirring, allowing to cool and standing (in all) three hours, the yarn is taken out, squeezed, and each portion treated with 200 c.c. of basic ferric sulphate of 1.5° B. (1.01 sp. gr.) in a beaker. After stirring for fifteen to twenty minutes the yarn is removed, washed and the depth of the shade compared. Antimony salt may also be used. In a similar manner, comparisons may be made of samples at different prices (see also *Leipziger Farberzeit.*, 1896, 261).

#### ANILINE AND ANILINE SALTS.

The value of aniline preparations depends on the proportion of aniline and on neutrality. They must be as dry as possible, free from excess of acid or base and also from other organic compounds.

**Aniline Oil, Aniline.**—(a) Distillation test. 100 c.c. of the sample are distilled; at least 96 per cent. should come over between 180° and 184° C. The distillation must be conducted in a place free from draughts and over a naked flame. The contents of the flask must be in lively ebullition, but must not be overheated. If the aniline is bought to a type sample, the latter should also be distilled in a similar manner at the same time, in order to eliminate differences due to atmospheric variations.

(b) Titration with bromine solution in a similar manner to aniline salts (see below).

**Aniline Salt** (hydrochloride, tartrate, etc.).

*Aniline.*—(a) Titration with bromine solution (Welter-Vaubel). The method depends upon the quantitative conversion of aniline in strong acid solutions into tribromaniline by the action of a solution of bromine in caustic potash (potassium bromide + bromate) and the recognition of excess of bromine by potassium iodide starch paper.

The brominating solution is obtained by gradually adding 100 grammes of commercial bromine (94 to 96 per cent.) to a solution of 95 grammes of caustic potash (73 per cent. of KOH) in 300 to 400 c.c. of water, boiling gently for one hour and filling up to 2,000 c.c. This solution is standardised

against chemically pure aniline hydrochloride, dried over sulphuric acid to constant weight. 1 gramme of the pure aniline salt is dissolved to 1,000 c.c. and 100 c.c. of the solution (= 0.1 gramme of substance) is titrated with the above solution, after adding 25 to 50 c.c. of strong hydrobromic acid, until the solution just becomes yellow. Instead of pure hydrobromic acid, hydrochloric acid, to which 10 per cent. of hydrobromic acid has been added, may be used. The same yellow coloration is obtained. Pure hydrochloric acid may be also used, but potassium iodide starch paper must then be employed. For example, if 96 c.c. of bromine solution correspond to 0.1 gramme of chemically pure aniline salt, the percentage of aniline salt in the sample next titrated is given by a simple calculation. Thus if 10 grammes of the sample are dissolved to 1,000 c.c., then 100 c.c. diluted to 1,000 c.c. and 100 c.c. of the last solution require 90 c.c. of bromine solution, then  $96 : 0.1 = 90 : x$ , or  $x = 0.09375$ , corresponding to 93.75 per cent. of aniline hydrochloride.

The method is very accurate, giving results agreeing to 0.1 per cent.

(b) The aniline may also be roughly determined in the following manner (Nölting, *Anilinschwarz*). In a stoppered graduated cylinder, 20 grammes of aniline salt, dissolved in 40 c.c. of hot water, are well shaken with 7 grammes of caustic soda (dissolved in 20 c.c. of water) and 30 grammes of common salt. After cooling, the volume is made up with water to 200 c.c. and the volume of the separated oil read off. The percentage by weight of aniline is obtained by multiplying by 5.13.

(c) 200 to 300 grammes of aniline salt are decomposed with caustic soda, the oil separated, dried by means of calcium chloride and distilled as given under *Aniline Oil* (see above).

*Estimation of Acid.*—(a) The acid may be determined by ordinary analytical methods. For example, in aniline hydrochloride, the hydrochloric acid can be precipitated by silver nitrate in nitric acid solution; in aniline tartrate, the tartaric acid can be estimated as in tartar, after separation of the aniline oil (see *Tartar*). The excess or deficiency of the acid is then calculated from the percentage of aniline oil.

(b) Knecht and Rawson proceed as follows: In each of three flasks, of 200 c.c. capacity, are placed 100 c.c. of water and 1 c.c. of a 0.1 per cent. solution of crystal violet; to two of these flasks (No. 1 and No. 2) are added 50 grammes of the sample of aniline salt, the third flask serves for comparison, as also No. 2. Flask No. 1 is then titrated with  $\frac{1}{10}$  N caustic soda until the solution, at first blue, again becomes a violet similar to No. 3.

(c) The aniline salt solution may also be directly titrated with standard caustic soda and litmus tincture to incipient blue coloration. Phenolphthalein is not as suitable.

*Free Hydrochloric Acid.* - Excess of free hydrochloric acid in aniline hydrochloride is recognised by the reaction given by filter paper saturated with a 0.1 per cent. solution of magenta or methyl violet; magenta paper is decolourised by excess of acid, whilst methyl violet is turned green.

*Free Aniline.* - Free aniline is detected by means of neutral copper sulphate, which imparts a greenish-brown coloration, whilst aniline salt remains colourless. It may also be detected and estimated by congo red. This method depends on the property of congo red, which has been turned blue by a trace of acid, of being again turned to red by free aniline. In the estimation, titration with  $\frac{1}{10}$  N acid is accordingly continued until the blue coloration begins to appear.

Water may be estimated by drying several grammes over sulphuric acid to constant weight.

For the estimation of toluidine in aniline and *vice versa* see *Zeits. anal. Chem.*, 1895, xxxiv., 734.

*Application.* On an extensive scale in the production of aniline black (direct black, oxidation black, steam black, etc.), in dyeing and printing "Aniline for blue" is pure aniline, "aniline for red" is a mixture of aniline and toluidines.

### THICKENING AND STIFFENING MATERIALS.

**Starch** is generally prepared from potatoes, wheat, maize, cassava, sago, tapioca and rice.

Starch is composed of minute grains which vary in appear-

ance according to the plant from which it is derived, it is a carbohydrate of the formula  $C_6H_{10}O_5$ , and when acted upon by acids is converted first into dextrin and then into glucose (dextrose).

Starch is insoluble in cold water, but on heating with water the granules expand and burst with the formation of a paste which solidifies to a jelly on cooling. The temperature at which starch thickens is not a definite one, some of the granules commence to burst at  $55^{\circ} C.$ , but the maximum stiffening takes place when all the granules have burst, this point is for wheat 65, maize starch 70, sago flour 72, rice starch 74, and potato starch 63.

The following are the microscopical characters of the most commonly occurring starches.

A. *Granules, Oval*.—Showing a well-marked cross under polarised light.

*Tous-le-mois or Canna Arrowroot*.—The granules of this starch are the largest of any of the commercial starches, being  $\cdot 0469$  to  $\cdot 132$  mm. in diameter. The concentric rings are well marked, and there is a distinct circular hilum or dot near the edge, the granule projecting in a point at this side.

*Potato*.—The largest granules are oyster-shaped and the smallest granules spherical, or nearly so. Size of granules  $\cdot 06$  to  $\cdot 1$  mm. diameter. The concentric rings are very conspicuous, and the circular hilum is at the broad end.

*Maranta or St. Vincent Arrowroot*. The granules of this starch resemble potato in shape but are much smaller, i.e.,  $\cdot 022$  to  $\cdot 06$  mm. diameter. The concentric rings are easily visible, and the hilum, consisting in most cases of a slit, is at the broad end or at one side near the centre.

There are several other varieties of arrowroot, but they are very little known in this country.

B. *Granules, Oval, with some Muller-Shaped or Flattened at one End*.—Showing a well-marked cross under polarised light.

*Sago*.—The granules are from  $\cdot 025$  to  $\cdot 066$  mm. diameter, the concentric rings are faintly visible and the hilum is circular, but there is in many cases a long slit passing through the hilum.



C. *Oval or Kidney-Shaped*.—Under polarised light one or more very distinct crosses are visible.

*Pea*.—The granules are often traversed with deep furrows so as to divide them into several portions, each of which shows a cross under polarised light. The size of the granules is  $\cdot 028$  to  $\cdot 066$  mm. diameter.

*Bean*.—This resembles pea starch except that the granules are more regular in size, the larger granules predominating. The size of the granules is  $\cdot 02$  to  $\cdot 075$  mm. diameter.

D. *Circular*.—Showing a very faint Maltese-shaped cross under polarised light.

*Wheat*.—The granules vary very considerably in size, i.e., from  $\cdot 0022$  to  $\cdot 052$  mm. diameter, the concentric rings are almost invisible. There is no hilum.

*Barley*.—The granules resemble those of wheat except that there are more of the intermediate-sized and many very small granules, they vary in size from  $\cdot 0018$  to  $\cdot 07$  mm. diameter; the concentric rings are slightly more visible; there is no apparent hilum.

*Rye*.—This resembles wheat and barley starch except that the large granules are larger than either, and there is often a stellate slit in the centre of these granules. The size of the granules varies from  $\cdot 0022$  to  $\cdot 08$  mm. diameter.

E. *Circular, with some Granules Flattened on the one Side*.—Showing a well-marked cross under polarised light.

*Tapioca*.—The granules in tapioca starch are small and fairly regular in size, being  $\cdot 014$  to  $\cdot 028$  mm. diameter. The concentric rings are visible and the hilum is very marked, being circular or mostly a slit or star-shaped.

*Cassava*.—This resembles tapioca starch.

F. *Angular Showing a well-marked Cross with Polarised Light*.

*Indian Corn or Maize*.—This starch varies from  $\cdot 02$  to  $\cdot 03$  mm. diameter. It shows a distinct star-shaped hilum in most cases.

*Rice*.—This is composed of extremely small granules, very regular in size, i.e.,  $\cdot 005$  to  $\cdot 0076$  mm. diameter. The granules shine brilliantly under polarised light, but the cross is so small that it is difficult to distinguish.

A direct quantitative estimation of the percentage of starch is hardly ever required for technical purposes in the textile industries, since it gives no criterion of the applicability and source of the material. This estimation is therefore not described; details may be found in Fresenius, *Quant. Anal.*, II. 459, 479 and other analytical text-books. The principle of the process is, the starch is first made into a paste, then brought into solution by means of malt extract (diastase), converted ("inverted") by means of hydrochloric acid into dextrose, and the latter estimated by the reduction of Fehling's solution, gravimetrically (Allihn) or volumetrically (Sohxlet).

*Microscopic examination* is of the first importance, and quite unavoidable if it is desired to form a comprehensive opinion of the sample. Owing to the characteristic form and the different dimensions of the grains of the various varieties of starch, it is not difficult, not only to distinguish qualitatively between the different varieties, but also to obtain a certain idea of the purity and uniformity of the material, since inorganic and organic impurities or admixtures, such as sand, mould spores, products of decomposition, etc., etc., may be detected with certainty in this manner. The microscopic appearances of the different starch grains are represented in the figures 10 to 20. For further information special works should be consulted.

*Water.*—Of great importance is also the amount of water, which increases considerably when the starch is stored, and may reach as high as 35 per cent. The quantity of water in potato starch varies from 15 to 18 per cent., and in wheat starch 14 to 16 per cent. according to conditions.

(a) In order to estimate the water, 10 grammes of starch are first dried for one hour at 40° to 50° C., then for four to five hours at 120° C., and weighed after cooling in the exsiccator. The loss in weight gives the proportion of water.

(b) For works where the determination in question is frequently made and several control determinations have to be done in succession, the alcohol method of Scheibler (*Drugg. Polyt. Journ.*, xcii., 504) is to be recommended, although it makes no claim to absolute accuracy.

The method is based upon the empirical fact that, when 1 part of starch containing 11.4 per cent. of moisture and 2 parts of alcohol of 90 per cent. by volume are mixed, neither takes up water from the other, thus in a sense both are equally hygroscopic; moister starch loses water and dilutes the alcohol; drier starch becomes wetter and the alcohol more concentrated. According to Scheibler, 41.7 grammes of starch are weighed into a glass vessel with an air-tight stopper, 100 c.c. of alcohol of 90° Tr. (90 per cent. by volume) added, the mixture frequently shaken during one hour, filtered through a dry filter and the specific gravity of the filtrate taken. The percentage of water in the starch is then taken direct from the following table —

| Water in Starch,<br>per cent. | Tralles. | Water in Starch,<br>per cent. | Tralles. | Water in Starch,<br>per cent. | Tralles. |
|-------------------------------|----------|-------------------------------|----------|-------------------------------|----------|
| 0                             | 93.3     | 14                            | 89.1     | 28                            | 84.6     |
| 1                             | 93.1     | 15                            | 88.7     | 29                            | 84.3     |
| 2                             | 92.9     | 16                            | 88.3     | 30                            | 84.0     |
| 3                             | 92.6     | 17                            | 88.0     | 31                            | 83.7     |
| 4                             | 92.3     | 18                            | 87.7     | 32                            | 83.4     |
| 5                             | 92.0     | 19                            | 87.4     | 33                            | 83.1     |
| 6                             | 91.7     | 20                            | 87.1     | 34                            | 82.8     |
| 7                             | 91.4     | 21                            | 86.7     | 35                            | 82.5     |
| 8                             | 91.2     | 22                            | 86.4     | 36                            | 82.2     |
| 9                             | 90.9     | 23                            | 86.1     | 37                            | 81.9     |
| 10                            | 90.5     | 24                            | 85.8     | 38                            | 81.6     |
| 11                            | 90.1     | 25                            | 85.5     | 39                            | 81.3     |
| 12                            | 89.8     | 26                            | 85.2     | 40                            | 80.9     |
| 13                            | 89.5     | 27                            | 84.9     | 50                            | 78.1     |

*Ash.* Important conclusions as to the purity of the sample may occasionally be drawn from an estimation of the ash. The ash in naturally pure starch ranges from .09 to 0.5 per cent. If starch is adulterated with sand, gypsum, chalk, barytes, clay, etc., these substances will be found in the ash. The starch may also be brought into solution by means of malt extract, when the above mineral impurities remain undissolved and may be further examined. According to Cailletot, 4 to 5 grammes of finely powdered starch are shaken with chloroform. The specifically lighter starch

(sp. gr. 1.4) rises to the surface, whilst most adulterants—which have a greater specific gravity than chloroform (1.526)—sink to the bottom.

*Organic impurities* may consist, according to Curdes, of coal-dust, dust, residues of potato skin, mould spores, dead algae, particles of wood, etc. These all remain undissolved when the starch is brought into solution by means of malt extract. A less valuable starch is the only organic adulterant to be considered; it is detected by means of the microscope.

The presence of *gluten* is occasionally important. It is recognised, according to Bottger (*Polyl. Notizbl.*, 1869, No. 15) in the following manner: 1 gramme of starch is heated to boiling with 180 c.c. of water, stirring well with a glass rod. If the starch contains gluten, the foam remains when boiling is stopped; if gluten is absent the foam disappears with the cessation of ebullition. The proportion of gluten may be determined by estimating the proportion of nitrogen. pure starch is free from nitrogen, which element is contained in gluten.

*Technical Examination.*—In addition to the above preliminary tests, practical tests are generally made, according to the purpose for which the starch is required. In this respect are to be considered: the thickening or stiffening capacity of the starch, its tendency to turn sour, and its general effect upon dyes and fibres.

*Thickening and Stiffening Test.*—A paste and a thinner solution are made of the starch to be examined and of standard samples, comparative trials of thickening or stiffening are then made by means of dressing and padding.

J. Wiesner (Wagner's *Jahresberichte der chem. Tech.*, 1868, 460) conducts the trials as follows:—For each sample of starch, twenty to thirty threads of cotton of medium size, about 50 cms. long (of finer yarn somewhat shorter, of coarser somewhat longer threads must be taken), are accurately weighed together, each separate thread is then drawn through the starch paste, *uniformly* stripped between the fingers and hung up to dry in an exactly vertical position at the room temperature. The second series of twenty to thirty threads is treated in exactly the same manner with the standard

starch, similarly a second, third, etc., sample. The threads, which it is most important not to crease or bend either before or after drying, are then fixed, one at a time, in a clamp in such a manner that at first only a short length of the thread projects upwards above the clamp. The thread is then raised by degrees, being clamped after each rise, until the thread finally falls over by its own weight to one side, so that the extremity lies in the same horizontal plane with the point of support in the clamp. Creased or broken threads are rejected. The length of each thread is then accurately measured from the extremity to the point at which it was clamped and the average length calculated. The threads are then accurately weighed and thus the weight of adherent starch obtained. The stiffening capacity is inversely proportional to the weight of starch and directly proportional to the length of the thread.

*Example :—*

| Starch.  | Average<br>length.    | Average Weight of Starch<br>on the Thread. |
|----------|-----------------------|--|
| <i>a</i> | <i>l</i>              | <i>w</i>                                   |
| <i>b</i> | <i>l</i> <sub>1</sub> | <i>w</i> <sub>1</sub>                      |
| <i>c</i> | <i>l</i> <sub>2</sub> | <i>w</i> <sub>2</sub>                      |
| <i>d</i> | <i>l</i> <sub>3</sub> | <i>w</i> <sub>3</sub>                      |

The stiffening capacities are then in the following ratios :—

$$a : b :: \frac{lw_1}{l_1w}; \quad a : c :: \frac{lw_2}{l_2w}, \text{ etc., thus if } a \text{ be taken as unity, } b = \frac{l_1w}{lw_1}, \quad c = \frac{l_2w}{lw_2}, \quad d = \frac{l_3w}{lw_3}.$$

The method necessitates very tedious labour and a careful choice of uniform threads, if reliable results are to be obtained.

*Keeping Capacity.*—50 grammes of starch are boiled with 1 litre of water, the volume made up to 1 litre, and the solution allowed to stand for several days. The starch, which remains fresh for the longest time, is *ceteris paribus* the best, that which first turns sour and ferments, or exhibits other signs of bacterial decomposition, is the least valuable.

*Dyeing Test.*—Pure white material (for wheat starch) or fabric dyed in sensitive colours (benzopurpurin, Turkey red,

logwood black) are treated with the starch in question on the padding machine, dried and examined. Attention is to be paid to the general appearance, "feel," the stiffening produced, the action on the dye, etc.; comparative trials may also be required.

*Application.*—In printing, especially calico-printing, also on an equally extensive scale in finishing.

**Prepared and Soluble Starch.** A large number of preparations of starch come into commerce under various names, partly as substitutes for gum and size, partly for starch. The majority consist of ordinary starch converted into a soluble form by mechanical or chemical treatment. They are also known as "soluble starch," "vegetable size," etc.

These substances, which differ greatly, are generally prepared by treating starch with superheated steam under pressure, with acids (sulphuric, hydrochloric), with caustic soda, with chlorine, etc. Thus the resulting products may contain the most varied admixtures and impurities, which may be very harmful to the fabrics on which the starch is used. On this account such preparations should never be employed without previous examination. The consumer should convince himself of the harmlessness of the substance by analysis (acids, caustic soda, chlorine) or by a number of carefully performed practical tests. Of a vast number of these preparations only a few may be briefly mentioned.

*Soluble starch*, obtained by heating starch with water in autoclaves for thirty to sixty minutes, at a pressure of 2 to 3 atmospheres, is a more or less clear gummy mass, which has to a great extent lost the thickening properties of starch.

*Apparatin* is a clear gummy mass, soluble in water, obtained by boiling starch with caustic soda and then neutralising the excess of soda with sulphuric acid. 60 kilos. of potato starch + 200 litres of water + 12 kilos. of caustic soda of 36° B. (diluted with 60 litres of water) are boiled together. The product is recommended especially for cotton and mixtures of cotton and wool.

*Chloin* generally contains free chlorine; it is obtained by the action of bleaching powder on starch. 150 parts of

starch are treated with 100 parts of bleaching powder solution of 5% B. and 1,750 parts of water at 60° to 70° C., or at the boiling point for ten minutes. The commercial preparation should be rejected, but it is said to be most suitable for felt, woollens and woollen mixtures.

*Starch powder* also comes into the market in a soluble form. This is a preparation obtained by the action of chlorine, hydrochloric acid or sulphur dioxide on starch; it is sold both in the form of paste and powder.

*Irish Moss.* This is made from a species of seaweed (*Chondrus crispus*) which grows profusely on the Irish coast. The plant easily breaks down on heating with water, forming a pale-yellow soft paste which has a characteristic smell. It contains a large amount of mineral matter. Irish moss extract is used for stiffening and finishing linens, etc.

*Algin.* This is made from seaweed by boiling with weak alkalis according to the process of E. C. C. Stanford. It occurs in the form of thin scales of a yellowish colour.

*Blandula* is a similar product but much darker in colour.

*Agar-agar* and *Japanese isinglass* are also made from seaweed. They are used to a limited extent in finishing.

*Gum Tragacanth.* This is a jelly obtained from seeds, and manufactured by the Gum Tragacanth Supply Co., Ltd. It is practically a pure carbohydrate ( $C_6H_{10}O_5$ ), but it differs in its constitution and properties from starch and all other forms of gum. Thus it consists of two carbohydrates—mannan and galactan—which yield mannose and galactose on hydrolysis. This material is used in sizing and finishing, and for a variety of other purposes.

*British Gum or Dextrin.* This material is prepared by roasting starch with or without the addition of a little nitric acid, to a temperature ranging in the first case from 210° to 280° C. and in the latter from 110° to 150° C. The products vary very considerably in their properties. White dextrin, sometimes known as soluble starch, is formed at the lower temperatures, and is of a cream colour. It resembles unaltered starch in appearance, but is partially soluble in cold water, the residue being unaltered starch. On heating with water it dissolves entirely to a viscous fluid, which re-

duces Fehling's solution and gives a violet-blue colour with iodine. The pale yellow dextrin, known as "canary," is made at the medium temperatures, and is more freely soluble in cold water, leaving little or no residue. It reduces Fehling's solution more strongly than the preceding, and yields a violet colour with iodine. Yellow dextrin is of a yellowish-brown colour, and is formed at the higher temperatures. It is freely soluble in cold water, reduces Fehling's solution strongly, and gives a red colour with iodine.

Dextrin forms with water a gummy solution, but it is much less viscous than with gum-arabic. When used for gumming purposes it requires to be dissolved in the proportion of about 2 parts of dextrin to 3 parts of water. Dextrin is employed for thickening calico-printers' colours, for stiffening fabrics, and as an ingredient in finishing materials.

Good dextrin should not be hygroscopic, but should be dry, odourless, with a slight insipid taste (not sweet maltose), readily friable, soluble in an equal volume of water, insoluble in alcohol and of 1.5 specific gravity. It must give with water a solution as colourless, clear and neutral as possible, which is not coloured blue by iodine solution (starch), not rendered turbid by lime water (oxalic acid), not precipitated by tannic acid and baryta water (soluble starch), or by lead acetate (gum-arabic, vegetable mucilage), and only slightly reducing Fehling's solution (maltose). Quantitative estimations may be made of maltose, by reduction of Fehling's solution; starch, as organic matter insoluble in water; sand and mineral constituents, as ash (the ash of pure dextrin should not appreciably exceed 1.0 per cent.); excess of water, by drying 20 to 30 grammes at 110° to 115° C. (the water should not exceed 13 per cent. at the most); and the acidity, by titration with  $\frac{1}{10}$  N caustic soda. A microscopic examination must also be undertaken mounting the material in alcohol. The keeping capacity may also be tested, as with starch, and the proper practical tests, which indicate the applicability of the material for various requirements, should be carried out (*Zandruaenfabrikation*, p. 51).

*Application.*—In printing and finishing.

*Gum-Arabic.*—The name gum-arabic is applied to a gum



which is exported from Aden and Bombay, etc., and is used for a variety of purposes. It is the product of various species of *Acacia*, hence the name gum acacia by which it is also known. The finest gum comes from *Acacia Senegal*, a native of Upper Egypt, the Soudan and Kordofan, where it is known as "hashab," and from whence it is sent to Aden and other African ports. Gum Senegal is obtained in the French colony of Senegal from the same tree, but is not so good in quality. Other gums resembling gum-arabic are "tall" gum from *Acacia seyal*, Morocco or Mogador gum from *Acacia arabica*, or *Acacia gummafera*, Abyssinian gum from *Acacia abyssinica*, or

*Acacia glaucophylla* and wattle gum, from several species of wattle trees growing in Australia, and Cape gum from *Acacia horrida* (Doornboom). There are several gums obtained in India from various trees, e.g., *Acacia arabica*, *Acacia catechu*, *Anogeissus latifolia*, *Odina rodriei*, *Prunus eburnea*, *Bauhinia retusa*, but they are of very little importance and are only used locally, with the exception of the gum from *Anogeissus latifolia*, which is known as "Ghati" or "Gatty" gum, and is exported to some extent, it being rather valuable owing to the high viscosity of the solution.

Gum-arabic is usually collected by wandering natives who carry it in skins to the merchants in the larger towns and villages, from whence it is sent to Aden and Bombay for shipment to Europe. It is usually more or less mixed with other gums, hence it is hand picked into various grades, of which there are quite a number, and the prices of which vary with the quality. Gum-arabic is also known according to its origin as picked Turkey gum, white Senaar, Senegal gum, Cape gum, Mogador or Morocco gum, Indian or Gatty gum, brown Barbary, and wattle gum.

Gum-arabic occurs usually in spherical or nearly spherical pieces, also in angular and sometimes in vermiform particles. It varies from colourless or white to various shades of yellow, wine red or brown, it is transparent except in the larger pieces which are rough on the outside or covered with minute cracks which are produced by the so-called bleaching in the sun. The gum is very brittle, the

fracture being angular and very glassy. Gum-arabic dissolves slowly in water to form a thick viscous solution; the solution made with cold water being thicker than with hot. It is insoluble in alcohol, and is precipitated by alcohol from its solution. Tannic acid gives a precipitate with a solution of gum-arabic, and the latter forms a solid white opaque jelly with basic lead acetate solution. Borax thickens the solution, while Fehling's solution shows no reduction on boiling. Iodine gives no colour with the gum. Gum-arabic contains about 12 per cent. of water and 2 to 3 per cent. of ash, consisting mostly of the carbonates of potash, lime and magnesia. It is usually regarded as a compound of arabic acid with potash and lime, but the constitution of arabic acid is somewhat problematical. On heating with nitric acid it yields mucic acid, and with sulphuric acid it is hydrolysed to galactose and arabinose; it therefore contains both galactan ( $C_6H_{10}O_5$ ) and araban ( $C_6H_8O_4$ ).

The quality of gum-arabic is judged by its colour, solubility in water, thickness or viscosity of its solution, adhesive properties, and freedom from impurities.

Gum-arabic should consist of irregular shining and brittle lumps of a white to wine-yellow or pale brown colour, generally traversed by cracks in the interior. It should readily powder and be not at all hygroscopic, show a shining conchoidal fracture and give with water an almost clear, thick viscous solution, which produces threads. The solution should not be slimy or gelatinous, it may have only a slight acid reaction and must be very adhesive. The taste must be slight and mucilaginous.

Gum-arabic is frequently adulterated by insoluble cherry gum, dextrin, etc., and bleached with sulphurous acid. In the latter case sulphuric acid can be detected. It is also often adulterated with the less valuable Senegal gum, or the latter is sold directly as gum-arabic.

For printing purposes it must be quite free from sand and the solution must not turn sour. The keeping capacity should be tested as with starch. 100 grammes of gum dissolved in 1 litre of water should give a solution of about 5° B. The ash should be not more than 4 per cent.

*Application.*—In printing, especially in the Mulhouse cotton industry on a great scale; also in finishing; in printing on silk.

**Gum Senegal** is the product of the same tree (*Acacia Senegal*) growing in the French colony of that name. As compared with gum-arabic it forms larger and more transparent spherical lumps, more rarely exhibits cracks, which however then reach to the interior, and frequently has in the interior large pear-shaped air bubbles. Externally it is rougher and less shining, white to reddish-yellow in colour; it shows a large conchoidal fracture of high lustre.

According to Liebermann (*Chem. Zeit.*, 1890, 665; *J. S. C. I.*, 1890, 770; 1893, 66) gum Senegal forms lumps of dull appearance, somewhat like etched glass, which, however, are shining and transparent in the interior. The lumps are generally longish, straight or twisted, cylindrical, annulated like a worm, and thus somewhat mulberry-shaped. Gum Senegal can accordingly be distinguished from gum-arabic by external appearance alone.

Further, it differs from gum-arabic in giving only a slight turbidity with mercurous nitrate and in being considerably thickened by borax, it is soluble in water with more difficulty, more slimy and gelatinous—thus of less binding power—and is more readily curdled by many reagents. The last property explains the smaller worth of gum Senegal as compared with gum-arabic. Other soluble gums, as “tali,” wattle, etc., resemble gum-arabic but have very little adhesive properties.

*Application.*—As a thickener similarly to gum-arabic.

**Gum Tragacanth.**—Gum tragacanth is the product of several species of *Astragalus* (*A. ascendens*, *A. leioclados*, *A. gummifer*, etc.), which grow in Syria, Asia Minor, Armenia and Persia, also to some extent in Turkey and Greece, especially in the mountainous parts of these countries. The gum is obtained by making incisions in the stems of the shrubs, the form of the gum being directly attributable to the shape of the incisions, thus “leaf” gum is obtained by longitudinal cuts, “thread” or “vermicelli” gum is obtained from punctures, while irregular cuts

result in rounded pieces or lumps which are not of much value. The chief ports from which tragacanth is exported are Basra on the Persian Gulf and Smyrna.

Tragacanth is not soluble in water, but swells up in that liquid in the cold, or better when hot, to form a thick paste, a 5 per cent. paste being quite stiff. On heating with weak acids (acetic, etc.), it gives a thinner jelly, as also when heated with water under pressure. Hydrogen peroxide also renders the gum thinner, but it is doubtful if this is an advantage. Heated with dilute sulphuric acid it yields the same sugars as gum-arabic does, *i.e.*, arabinose and galactose, it is therefore also a gum of the galactan-arabin type. The essential principle of this gum was until recently known as bassorine, and the formula assigned to it was  $C_6H_{10}O_5$ , but this is not the case, the gum being a complex containing both  $C_6H_{10}O_5$  and  $C_6H_8O_4$  in intimate combination. The amount of water in tragacanth varies with the state of the atmosphere, *i.e.*, from 12 to 29 per cent., and it contains 3 to 5 per cent. of ash consisting of the carbonates of lime, magnesia and potash.

There is a variety of gum resembling tragacanth to some extent in its properties, known as "hog-trag". This occurs in thicker leaves or rounded or irregular lumps, white, yellow, or brown and opaque. It yields a paste more like starch and has a distinct characteristic odour. This gum is very much lower in price than the genuine tragacanth.

**Gum tragacanth** comes into the market in crinkled, flat, shell-shaped pieces or in form resembling vermicelli. It should be without smell and taste, transparent, bony and tough, so that it is very difficult to powder. Only a small portion dissolves in water, the greater part swelling up to mucilage, which is not sticky though adhesive. Under the microscope, swollen cell-like structures are visible containing in their centres a few small angular starch granules which give a faint violet colour with iodine solution.

It ought not to become sour too quickly and should contain not more than 6 per cent. of mineral matter (ash).

Bombay gum, cherry gum (cerasin), etc., are insoluble gums which may be used for adulterating tragacanth: they

are of no value. Gum-arabic is sometimes used for adulterating powdered tragacanth. It can be detected by the blue colour yielded with guaiacum tincture. (Test for oxydases.)

A technical experiment must be employed in order to evaluate tragacanth; the stiffening property is the most important (see stiffening property under *Starch*).

*Application.*—In combination with potato and especially wheat starch (with which it works better), size, dextrine, etc., it is much used in finishing silk (France), and silk mixtures, also for other fabrics. It is also used by printers, who often boil the tragacanth six to ten hours in order to obtain complete division through the water.

A cheap substitute for tragacanth is proposed by Boscian: 20 parts of starch, 6 parts of size and 2 parts of glycerin are vigorously boiled together in water.

**Glue, Size.**—A distinction is made between hide, bone and fish glue. Gelatine is purified and bleached bone glue, it is examined in a similar manner to the crude glues, with the addition that regard must be paid to its colour and to substances which might be introduced in bleaching (sulphuric acid by sulphur dioxide, etc.). Hide glue has greater adhesive power than bone glue.

In the first place glue must be free from acid (hydrochloric, etc.) and from the alum used in clearing it. Good glue is also not too dark in colour, although very brittle it is broken with difficulty, has only a slight elasticity and is not hygroscopic. The fracture should shine like glass; a splintery fracture indicates incompletely dissolved sinewy parts. Good glue should not alter in shape in cold water; it should simply swell considerably and not even be liquid after forty-eight hours (good hide glue, however, liquefies to some extent). At 28° C. the swollen glue begins to melt and is quite fluid at 50° C. The adhesiveness of a glue is greater the less its solution has been heated and the fresher the materials employed in its preparation.

Glue should have no salty or acid taste. If an accurately weighed quantity of glue be left in cold water for twenty-four hours, and then again dried, the glue which approaches most nearly to the original weight is the best.

The following estimations may also be made.—

*Water*.—2 to 3 grammes of finely rasped glue are dried at 110° to 115° C. to constant weight.

*Ash*.—An examination of the ash will decide whether the material is a hide or bone glue. The ash of the latter melts in the Bunsen flame, its aqueous solution is neutral, it contains phosphoric acid and chlorine. The ash of hide or leather glue is infusible in the Bunsen flame, contains much caustic lime, is strongly alkaline and generally free from phosphoric acid and chlorine.

*Acid*.—80 c.c. of water are poured over 30 grammes of glue and allowed to stand several hours. The volatile acids are then driven over in steam, caught in a receiver and when 200 c.c. have distilled, titrated.

The drying capacity, foreign matter, smell, etc., may also be tested. For further information see Bockmann, *Zundwaaren*, p. 533 *et seq.*; C. Stelling, *Chem. Zeit.*, 1897, 47, 461.

*Practical Test*.—In addition to the above examination, several finishing experiments should be made, as indicated under the head of starch. Silk mixtures and woollen goods are the best for the purpose. A sensitive benzidine (benzo-purpurin) dye, aniline black or logwood black, is suitable.

*Application*.—Very extensive in finishing, less in printing and dyeing (brightening silk).

#### • DYES.

To deal with the subject of dyes exhaustively lies outside the scope of this work. The subject is sufficiently immense to require a separate treatise, there already exist numerous excellent books, sufficient for every requirement, treating of the dyes as to their manufacture, composition and application, whilst the literature of the subject increases very largely year by year. In this place it is merely necessary to indicate very briefly the origin of and characters of the dyes and the manner of examining them chemically and for shade.

The dyes may be divided into two classes—1. The Coal Tar or Synthetic Dyes, and 2. The Natural Dyes.

### COAL-TAR DYES.

The raw material from which the coal-tar dyes are obtained is coal tar, but the intermediate product from which the original dyes were obtained was aniline, hence they were known as aniline dyes. Large numbers of dyes are now, however, made from other products derived from coal tar, such as phenol, naphthols, naphthalene, anthracene, etc.; hence it is more correct in speaking collectively of these dyes as coal-tar dyes. There is an enormous number of these dyes sold under different designations, but a very large proportion of these are mixtures of two or more dyes; of individual dyes it is computed that there are something like 1,000 of more or less value commercially.

Coal-tar dyes are usually well-defined compounds which may be divided into groups according to their constitution. The following method of classification is perhaps most convenient:—<sup>1</sup>

#### *Coal-tar Dyes.*

- A. Nitro colours.
- B. Monoazo colours.
- C. Disazo colours.
- D. Trisazo colours.
- E. Tetrakisazo colours.
- F. Nitroso or quinoneoxime colours.
- G. Stilbene or azoxy colours.
- H. Oxyketone, oxylactone and oxyquinone colours.
- I. Diphenylmethane colours.
- J. Triphenylmethane colours.
- K. Xanthene colours.
- L. Acridine colours.
- M. Anthracene colours.
- N. Indophenols, indamines, etc.

<sup>1</sup> *A Systematic Survey of the Organic Colouring Matters*, by Prof. A. G. Green, 1904, p. vi.

- O. Azines and azonium colours.
- P. Oxazine colours.
- Q. Thiazine colours.
- R. Thiazol or thiobenzene colours.
- S. Quinoline colours.
- T. Sulphide colours.

*Natural Dyes.*

- U. Indigo and derivatives.
- V. Other natural dyes, logwood, umach, etc.

A. *Nitro Colours.*—The nitro colours are prepared by the action of nitric acid upon phenols, amines, etc., and may be distinguished by containing the nitro group  $\text{NO}_2$ . They are all yellow or orange colours, *e.g.*, picric acid, naphthol yellow, etc., and although they will dye animal fibres without a mordant, the colours are more or less fugitive, some of them extremely so.

- B. *Monoazo colours.*
- C. *Disazo colours.*
- D. *Trisazo colours.*
- E. *Tetrakisazo colours.*

These are similar in character, since they all contain the azo group— $\text{N} = \text{N}$ —the monazo containing one, the disazo two, the trisazo three, and the tetrakisazo compounds four such groups. They are prepared by diazotising an amine and combining the diazo compound with an amine or phenol or its derivatives. The azo dyes containing free amido groups are basic in character, and dye cotton in conjunction with tannic acid; they also dye wool and silk without a mordant. Examples of these dyes are aniline yellow, chrysoidine, methyl orange. The sulphonated azo dyes dye wool from an acid-bath but are not suitable for cotton; acid yellow, cochineal scarlet, victoria violet, and acid brown are examples of this class. Certain of the azo dyes derived from benzidine, tolidine, etc., will dye cotton without a mordant, *e.g.*, chrysamine, diamine red, diphenyl brown, Congo red, and others are applied to wool after mordanting, *e.g.*, fast violet R, chrome black, anthracene yellow C, cloth orange, etc.

The monoazo dyes include: Aniline yellow, cochineal



scarlet, chrysoidine, alizarine yellow GG, victoria violet 4BS, wool scarlet R, diamine rose, resorcin yellow, brilliant yellow S, Clayton cloth red. The disazo dyes include: Acid brown, naphthol black, fast scarlet B, Bordeaux G, fast violet, chrome black, anthracene yellow, Bismarek brown, toluylene brown, diamine fast red, Congo red, diamine violet, anthracene red, benzopurpurine, Congo corinth, azo blue, diamine blue, azo violet, indazurine, Hessian purple. The trisazo dyes include: Oxamine violet, Crumpsall brown, direct indigo blue, benzo olive, direct black V, diamine green, alizarine yellow PS.

The tetrakisazo dyes include: Benzo brown, azo orange R, gambine, direct heliotrope.

F. *Nitroso or Quinonoxerime Colours.* This group of dyes contains the group NO, and all the dyes except naphthol green can be applied to wool and silk mordanted with chromium or iron. Naphthol green is a sulphonated dye which dyes from an acid-bath. The members of this group are very few in number, and they are all green. Examples: Fast green, gambine, naphthol green.

G. *Stilbene or Azory Colours.* These dyes are dis-

tinguished by containing the group  $\begin{array}{c} \text{N} \\ | \\ \text{O} \\ | \\ \text{N} \end{array}$  and dye cotton,

silk, and wool without a mordant. Examples: Sun yellow, mikado yellow, diphenyl fast brown G.

H. *Oxyketone, Orylactone, and Oryquinone Colours.*—The members of this group contain one or more ketone (CO) groups in association with two or more hydroxyls (HO). They have very little colouring power, but in association with chrome and iron mordants they yield extremely fast colours on cotton, silk, and wool. Alizarine yellow, alizarine dark green, and anthracene yellow belong to this group.

I. *Diphenylmethane Colours.*—These are basic colouring matters derived from diphenylmethane  $\text{CH}_2(\text{C}_6\text{H}_5)_2$ . They dye wool and silk direct and cotton after mordanting with tannic acid. Examples: Auramine, pyronine.

J. *Triphenylmethane Colours.*—These dyes are also basic

in colour, being derived from triphenylmethane  $\text{CH}(\text{C}_6\text{H}_5)_3$ , and in the dye-bath they behave similarly to the preceding. Examples: Malachite green, magenta, victoria green 3B, night blue, chrome green, Hofmann's violet, methyl violet, methyl green, alkali blue.

K. *Xanthene Colours*.—These contain one or more ketone groups (CO) and dye unmordanted silk and wool, or cotton prepared with tannic acid. Many of the dyes are beautifully fluorescent, e.g., eosine, erythrosine, rose Bengal, phloxine.

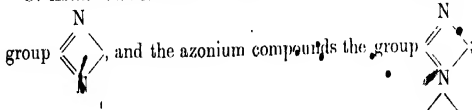
L. *Acridine Colours*. The acridine colours are character-

ised by containing the group  $\begin{array}{c} | \\ \text{C} - \text{N} \\ | \end{array}$  and are formed by condensation of an aldehyde with an aromatic amide, heating the product with acid, thus removing ammonia, and oxidising the resulting product. These dyes dye silk and wool without a mordant and cotton after mordanting with tannic acid. Examples: Acridine yellow, benzoflavine, phosphine.


M. *Anthracene colours* are derived from anthracene ( $\text{C}_{14}\text{H}_{10}$ ) and they contain one or more carboxyl (CO) groups. They are all very fast colours and dye wool mordanted with alum, they are also fixed on cotton with sulphonated oil or by means of alumina or chromium mordants. Alizarine, purpurine, alizarine brown, acid alizarine, anthracene blue, anthracene green, and indanthrene belong to this class.

N. *Indophenols, Indamines, etc.*—Indophenols contain the group  $\begin{array}{c} // \\ \text{N} \\ \backslash \end{array}$  and are dyed like indigo, first by reduction, to a leuco compound, and then by oxidation. Aniline black, an indanine (nigraniline  $\text{C}_8\text{H}_5\text{N}$ ), belongs to this group, produced from aniline by oxidation and formed directly on the fibre. These are extremely fast dyes.

O. *Azines and Azonium Colours*.—The azines contain the




they are formed by the combination of two colour bases, one being a nitroso and the other an amido compound, *e.g.*, nitrosomethylaniline and *m*-phenylene-diamine and in other ways. They are used mostly for dyeing cotton mordanted with tannic acid or for calico-printing, but some are suitable for dyeing silk. Some of these dyes are insoluble in water but are converted into soluble dyes by sulphonation, *e.g.*, indulines. Examples of dyes belonging to this class are: Neutral violet, safranine, methylene violet, mauve, induline, nigrosine, azine green, magdala red.

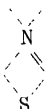
P. *Orazine Colours*.—These contain the group  and

are prepared in a variety of ways, mostly by condensation of nitroso compounds with amides. These dyes are employed for dyeing cotton after mordanting with tannic acid, also for calico-printing and to some extent for wool dyeing along with a mordant. The most important members of this group are Capri blue, gallocyanine, indalizarine, resorcin blue, Meldola's blue, Nile blue, alizarine green.

Q. *Thiazine Colours*.—These dyes are similarly constituted to the oxazines, but they contain sulphur in place of oxygen

; they are also used in the same way as the latter.

R. *Thiazol or Thiobenzoyl Colours*.—These products

contain the group  and dye cotton after mordanting

with tannic acid, but the tints are not very fast to light or alkali. Primuline—discovered by Prof. A. G. Green—belonging to this group, can be developed on the fabric by diazotisation and exposure to light, forming exceedingly brilliant and fast colours (ingrain colours). This discovery is due to Green, Cross, and Bevan, and is known as the "Diazotype process" of printing. Thioflavine, primuline, and Clayton yellow belong to this group.

S. *Quinoline Colours.*—These dyes, derived from quinoline,  $C_9H_7N$ , constitute a small group composed of the quinoline yellows, red, and blue or cyanine. The chief use of these dyes is for colour sensitising photographic plates.

T. *Sulphide Colours.*—These are a group of colours the constitution of many of which is quite unknown; they form very valuable dyes and are remarkable for the fact that cotton is dyed from an alkaline sulphide bath, in which the dyes are soluble, but they are quite unaffected by water and soap. Cachou-de-Laval, cotton black, cotton brown, cross-dye blacks, fast black, are members of this group.

#### NATURAL DYES.

*Indigo.*—Indigo is obtained from a leguminous plant (*Indigofera tinctoria* and many other species) which is cultivated on a large scale in India, Java, Kupah, Bengal, Assam, and Burma. It is obtained from the leaves and twigs of the plant by steeping them in water and beating the liquid so as to aerate it, when the indigo deposits. An alternative process is to allow the leaves to remain until they change to a blue-grey colour, then to steep and ferment them whereby the indican in the plant is changed into indigo and indiglucon. Indigo usually comes into commerce in the form of deep blue lumps which are insoluble in water. It is very variable in composition, containing from 20 to 90 per cent. of pure indigo (indigotin), but more usually 40 to 50 per cent., indigo red or indirubin 2 to 4 per cent., indigo brown, water 2 to 8 per cent., ash 8 to 20 per cent. and small quantities of other impurities.

On treatment with water and a reducing agent (lime and ferrous sulphate, zinc dust, etc.) it is reduced to indigo white which again oxidises to indigo blue on exposure to air. Fabrics are dyed in the reduced vat and then oxidised. It dyes wool, silk, and cotton and is entirely fast to light and soap.

*Indigotin* or *Synthetic Indigo* is an artificial coal-tar dye, but it can be prepared from indigo by sublimation with heat. It is the pure indigo blue  $C_{16}H_{10}N_2O$ , and up to recently was largely superseding the natural product.

*Indigo Extract* or *Indigo Carmine*.—This is a deep violet-blue coloured paste formed by the sulphonation of indigo with fuming sulphuric acid. It is freely soluble in water and dyes wool blue or violet-blue, but the colours although bright are not very fast.

*Logwood* or *Campeachy Wood* is the heart wood of *Hæmatoxylum campechianum*, a large tree which grows in British Guiana, Central America, Cuba, Hayti, Jamaica, etc. It is a red wood, the colour developing considerably on exposure to moisture and the air.

*Logwood Extract* is prepared by boiling the chips with water and evaporating the solution either to a syrup or to a solid, which is brownish black, glossy, and brittle.

Logwood is used for dyeing wool black with iron or chromium mordants, it also yields violet-blues and greys with alumina or tin mordants.

*Brazil Wood*, *Sappan Wood*, *Peach Wood*, etc. There are a great many red woods included under these names, but the true Brazil wood is the product of species of *Cæsalpinia* which grow in tropical regions, e.g., Central and South America, West Indies, Africa, and parts of Asia, etc. It yields brown or reddish-brown shades with bichromate on wool, blue shades with sulphate of alumina, and scarlet with stannic chloride.

The colouring matter of Brazil wood is Brazilein  $C_{22}H_{16}O_7$  which is produced by oxidation of Brazilin  $C_{22}H_{18}O_7$ .

*Camwood*, *Barwood*. These are obtained from species of *Pterocarpus* and *Baphia*, which grow in Africa, East Indies, and Ceylon. They are not much used; on wool they give claret-browns with bichromate, and on cotton red shades with aluminium and tin mordants.

*Madder* is the red colouring matter obtained from the madder plant *Rubia tinctoria*, which at one time was grown on a large scale in France and elsewhere. It yields the two colouring matters alizarine and purpurine, which are now made artificially and have entirely displaced the natural product. Alizarine and purpurine are mentioned under the coal-tar dyes.

*Cochineal*.—Cochineal is the dried body of the female

cochineal insect, *Coccus cacti*, which feeds upon the cactus plants in Central Mexico and the West Indies. It contains about 10 per cent. of a bright red colouring matter which is made into a lake known as carmine.

Cochineal along with a tin mordant yields a very brilliant scarlet or crimson dye on wool, which is fast to light but not soap.

*Orchil*, *Cudbear* or *Litmus*.—This is obtained from species of lichens belonging to the genus *Rocella* and *Lecanora* by extraction with water and evaporation to a syrup or to a solid on effalk in the form of cubes. The colouring matter is bluish-red, but changes to blue with alkalis and red with acids. It dyes wool or silk with or without a mordant, but the colour fades on exposure to light.

*Annatto*.—The fruit of *Bixa orellana*, growing in Central America, India, etc., contains an orange colouring matter which after extraction appears as a liquid or paste of an orange colour. It dyes orange shades on cotton, silk, and wool either from a soap-bath or with a tin mordant. In acid solution it yields a red colour. It is not much used in dyeing, its chief value being for colouring butter and cheese.

*Safflower* is the dried petals of *Carthamus tinctorius*. It dyes cotton and silk a pink colour from an alkaline bath and then again after acidifying, but the colour is very fugitive.

*Weld*.—This is obtained by extracting the plant known as dyers' rocket (*Reseda luteola*), a native of Europe, with hot water. It dyes silk and wool mordanted with aluminium sulphate or alum a yellow colour. The colours are moderately fast to light and soap.

*Old Fustic*.—The wood of *Morus tinctoria*, which grows in various parts of North and South America, yields a yellow colouring matter, which is employed in wool and silk dyeing, and with aluminium and tin mordants yields bright yellow colours, and with iron, copper, and chromium mordants various olive shades. The colours are not fast to light but they stand washing fairly well.

*Young Fustic* is the wood of *Rhus cotinus* which grows in the south and east of Europe, the Levant, and the West

Indies. It dyes wool a bright orange-yellow with stannous chloride as a mordant, and brown or olive with copper, iron, and chromium, but the colours, although fairly fast to soap, fade very quickly in sunlight.

• *Persian Berries*.--The dried unripe berries of various species of *Rhamnus* (*R. tinctoria*, *R. infectoria*, etc.) yield a yellow colouring matter which is used in wool dyeing and also in calico-printing. It gives a bright yellow with stannous chloride, and olive or brown with copper, iron, and chromium, the colours being fairly fast to light.

*Quercitron*.--The inner bark of *Quercus tinctoria*, or dyers' oak, which is native to North America, contains a yellow colouring matter which is extracted and sold under the name of "Flavine Yellow Shade". This consists for the most part of "quercetin". By the action of dilute sulphuric acid it is converted into a dyestuff having a redder shade; this is known as "Flavine Red Shade". Quercitron and flavine are used for dyeing cotton and wool. With stannous chloride as a mordant it yields bright yellow shades which are fairly fast to light and soap.

*Turmeric* is the root of a plant *Curcuma longa*, which is found in India, China, and the East Indies. It dyes both cotton and wool without a mordant, but the colours very quickly fade on exposure. It becomes brown in contact with alkalis, and when dried on paper with boric acid gives a bright red colour, changed to green with caustic soda, or blue with ammonia. This is a characteristic reaction both for turmeric and for boric acid.

*Indian Yellow* or *Purree* is a yellow colouring matter obtained in India from the urine of cattle which are fed upon the mango plant. It is used more particularly as a pigment, although it has some value as an indigenous dye in India.

*Cutch*, *Catechu*, *Gambier*, etc.—This is a dried extract obtained in the East Indies from several distinct trees, e.g., the betel nut or areca (*Areca catechu*), *Acacia Arabica* and species of *Uncaria*, trees allied to the cinchona group. It yields very fast browns on cotton or wool in conjunction with bichromate of potash and other mordants and is also employed for weighting silk.

The most important characters of a dye are its chemical composition, general character and properties, shade, strength or concentration, purity and presence or absence of other dyes.

The *chemical constitution* is ascertained by advanced synthetic and analytical methods, which require in the first place a systematic chemical training.

The *general character* is studied by means of trial dyeings on different fibres, by different methods and with various assistant materials. The dye fixed on the fibre is examined for fastness to light, air, washing, boiling, soap, water, acids, alkalis, rubbing, chlorine, sulphur, ironing, steaming and moisture, also for level dyeing, and possibility of using in conjunction with other dyes, etc.

The *shade* is ascertained by trial dyeings, using different percentages of dye, in comparison with similar and competing dyes in varying depths of hue, in combination with various dyes used for shading the principal dye, sampling by direct and indirect daylight, by gas light and electric light, etc.

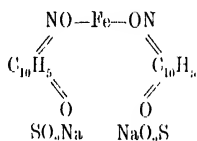
The *strength or concentration* is tested by quantitative dye trials against a standard, or occasionally colorimetrically.

The *purity and individuality* are ascertained by qualitative and quantitative estimations of the diluent and foreign colouring matter, intentionally or accidentally present. The following substances are most frequently used as diluents: Dextrine, sugar, starch, common salt, Glauber's salt, etc. Dyes diluted by these agents and containing as low as 3 per cent. of colouring matter come into the market, chiefly for export. The added substances may almost always be discovered as an insoluble residue by fractional solution of the dye in alcohol, ether, etc., and its proportion determined by weighing after drying, subsequently adding the natural moisture, for such material as starch and dextrin. The residue may then be examined qualitatively. Dextrin and salts, such as common salt and Glauber's salt, are soluble in cold water. Dextrin is precipitated on the sides of the beaker as a gummy mass on addition of excess of alcohol. The solution of dextrin reduces Fehling's solution on heating and



more strongly after heating with acid and neutralising. Common salt and Glauber's salt can be detected by the usual reactions. Sugar is also soluble in cold water, does not reduce Fehling's solution, but after heating with very dilute hydrochloric acid for only a few seconds it becomes inverted and then reduces Fehling's solution copiously. Starch is insoluble in cold water, but on heating with water forms a paste which, after cooling, gives a blue colour with iodine solution.

Salts are sometimes added to dyestuffs during the manufacture, to salt them out, either sodium chloride or sodium sulphate being most commonly employed. The presence of sodium sulphate in the ash of a dye does not, however, necessarily point to the addition of Glauber's salt, since many dyes, being sodium salts of sulphonated acid dyes, leave sodium sulphate on ignition. Thus naphthol green, being the ferrous sodium salt of nitroso- $\beta$ -naphthol- $\beta$ -mono-sulphonic acid,



after ignition would leave 24.8 per cent. of sodium sulphate and in addition 14.0 per cent. of ferric oxide.

It is frequently more difficult to discover the addition of a foreign colouring matter used to alter the shade. If the mixture has been made by bringing together the already dry colouring matters, the components may be recognised by dusting the very finely ground dye against wet filter paper. But if the mixture has been more thorough, *e.g.*, obtained by producing mixed crystals of the components, they are only discovered with much more difficulty, and at times only by an expert by means of a series of typical colour reactions.

# APPENDIX.

1917.

## International Atomic Weights.

|                  | Symbol. | Atomic Weight. |                                 | Symbol | Atomic Weight. |
|------------------|---------|----------------|---------------------------------|--------|----------------|
| Aluminium . . .  | Al      | 27.1           | Neodymium . . .                 | Nd     | 144.3          |
| Antimony . . .   | Sb      | 120.2          | Neon . . .                      | Ne     | 20.2           |
| Argon . . .      | A       | 39.88          | Nickel . . .                    | Ni     | 58.68          |
| Arsenic . . .    | As      | 74.96          | Nitron (radium emanation) . . . | Nt     | 222.1          |
| Barium . . .     | Ba      | 137.37         | Nitrogen . . .                  | N      | 14.01          |
| Bismuth . . .    | Bi      | 208.0          | Osmium . . .                    | Os     | 190.9          |
| Boron . . .      | B       | 11.0           | Oxygen . . .                    | O      | 16.00          |
| Bromine . . .    | Br      | 79.92          | Palladium . . .                 | Pd     | 106.7          |
| Cadmium . . .    | Cd      | 112.40         | Phosphorus . . .                | P      | 31.04          |
| Cæsium . . .     | Cs      | 132.81         | Platinum . . .                  | Pt     | 195.2          |
| Calcium . . .    | Ca      | 40.07          | Potassium . . .                 | K      | 39.10          |
| Carbon . . .     | C       | 12.005         | Praseodymium . . .              | Pr     | 140.9          |
| Cerium . . .     | Ce      | 140.25         | Radium . . .                    | Ra     | 226.0          |
| Chlorine . . .   | Cl      | 35.46          | Rhodium . . .                   | Rh     | 102.9          |
| Chromium . . .   | Cr      | 52.0           | Rubidium . . .                  | Rb     | 85.45          |
| Cobalt . . .     | Co      | 58.97          | Ruthenium . . .                 | Ru     | 101.7          |
| Columbium . . .  | Cb      | 93.1           | Samarium . . .                  | Sa     | 150.4          |
| Copper . . .     | Cu      | 63.57          | Scandium . . .                  | Sc     | 44.1           |
| Dysprosium . . . | Dy      | 162.5          | Selenium . . .                  | Se     | 79.2           |
| Erbium . . .     | Er      | 167.7          | Silicon . . .                   | Si     | 28.3           |
| Europium . . .   | Eu      | 152.0          | Silver . . .                    | Ag     | 107.88         |
| Fluorine . . .   | F       | 19.0           | Sodium . . .                    | Na     | 23.00          |
| Gadolinium . . . | Gd      | 157.3          | Strontium . . .                 | St     | 87.63          |
| Gallium . . .    | Ga      | 69.9           | Sulphur . . .                   | S      | 32.06          |
| Germanium . . .  | Ge      | 72.5           | Tantalum . . .                  | Ta     | 181.5          |
| Glucinum . . .   | Gl      | 9.1            | Tellurium . . .                 | Te     | 127.5          |
| Gold . . .       | Au      | 197.2          | Terbium . . .                   | Tb     | 159.2          |
| Helium . . .     | He      | 4.00           | Thallium . . .                  | Tl     | 204.0          |
| Holmium . . .    | Ho      | 164.5          | Thorium . . .                   | Th     | 232.4          |
| Hydrogen . . .   | H       | 1.008          | Thulium . . .                   | Th     | 168.5          |
| Indium . . .     | In      | 114.8          | Tin . . .                       | Sn     | 118.7          |
| Iodine . . .     | I       | 126.92         | Titanium . . .                  | Ti     | 48.1           |
| Iridium . . .    | Ir      | 193.1          | Tungsten . . .                  | W      | 184.0          |
| Iron . . .       | Fe      | 55.84          | Uranium . . .                   | U      | 238.2          |
| Krypton . . .    | Kr      | 82.92          | Vanadium . . .                  | V      | 51.0           |
| Lanthanum . . .  | La      | 139.0          | Xenon . . .                     | Xe     | 130.2          |
| Lead . . .       | Pb      | 207.20         | Ytterbium (Neoytterbium) . . .  | Yb     | 173.5          |
| Lithium . . .    | Li      | 6.94           | Yttrium . . .                   | Yt     | 88.7           |
| Lutecium . . .   | Lu      | 175.0          | Zinc . . .                      | Zn     | 65.37          |
| Magnesium . . .  | Mg      | 24.32          | Zirconium . . .                 | Zr     | 90.6           |
| Manganese . . .  | Mn      | 54.93          |                                 |        |                |
| Mercury . . .    | Hg      | 200.6          |                                 |        |                |
| Molybdenum . . . | Mo      | 96.0           |                                 |        |                |



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# DYERS' MATERIALS

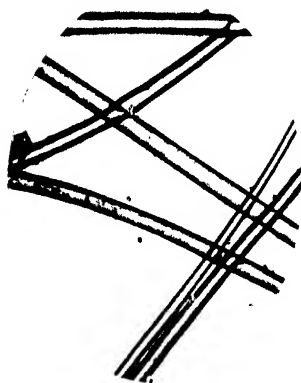


FIG. 1. W. 30. 50 100

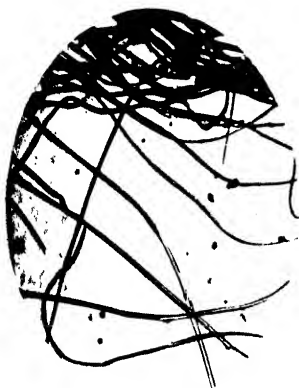


FIG. 2. W. 30. 50 100





DYERS' MATERIALS.



FIG. 3. COTTON  $\times 80$  DIA.

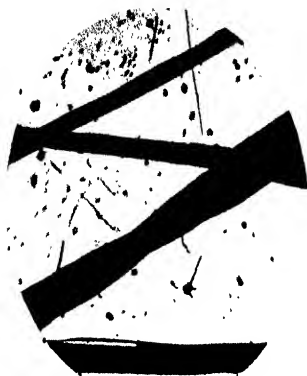


FIG. 4. RAMIE  $\times 80$  DIA.



DYERS' MATERIALS.



FIG. 5. LINEN  $\times$  80 DIA.



FIG. 6. JUTE  $\times$  80 DIA.



DYERS' MATERIALS.



FIG. 7. HEMP  $\times 80$  DIA.



FIG. 8. VISCOSE SILK  $\times 80$  DIA.



DYERS' MATERIALS.

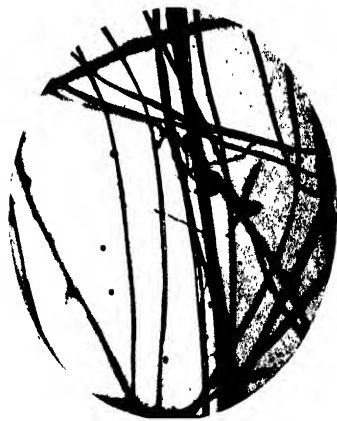


FIG. 9. CELLULOSE SILK  $\times 80$  DIA.

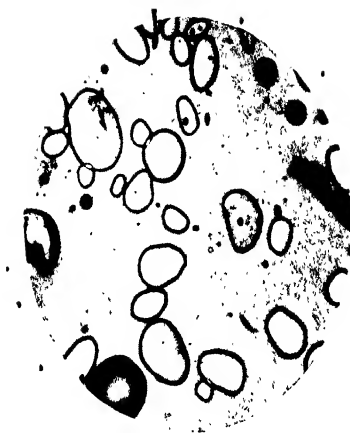


FIG. 10. TORUS-LE-MOULS  $\times 110$  DIA.





DYERS' MATERIALS.

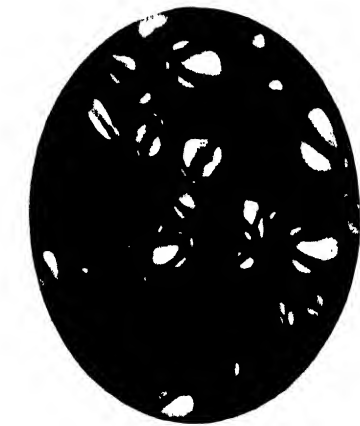


FIG. 11, TOUSSE-MOPS  $\times 110$  POLARISED LIGHT.

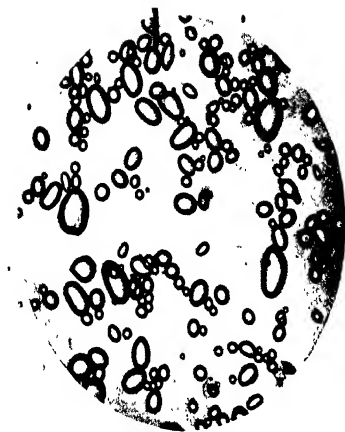


FIG. 12, POTATO STARCH  $\times 110$  DIA.



DYERS' MATERIALS.

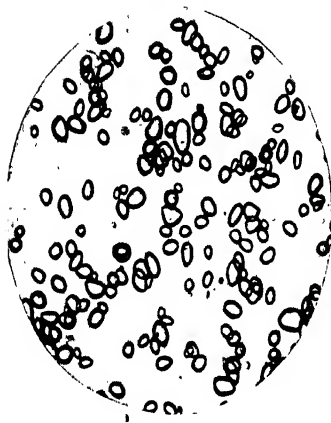


FIG. 13. S<sub>1</sub>. VINCENT ARROWROOT - 110 DIA.

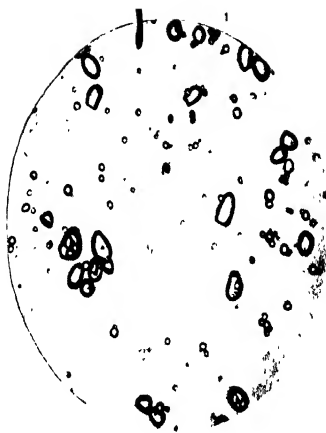


FIG. 14. S<sub>60</sub>. SAGITTARIA - 110 DIA.



DYERS' MATERIALS.



FIG. 15. PEA STARCH  $\times 110$  DIA.

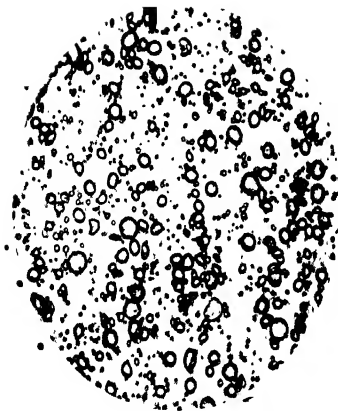


FIG. 16. WHEAT STARCH  $\times 110$  DIA.



DYERS' MATERIALS.

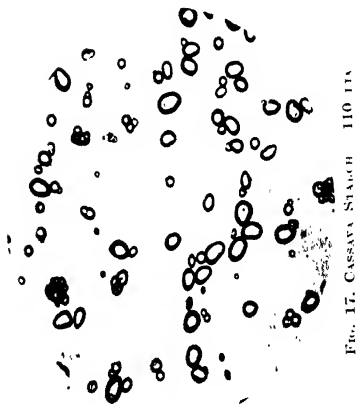


FIG. 17. CASSAVA STARCH 110 DIA

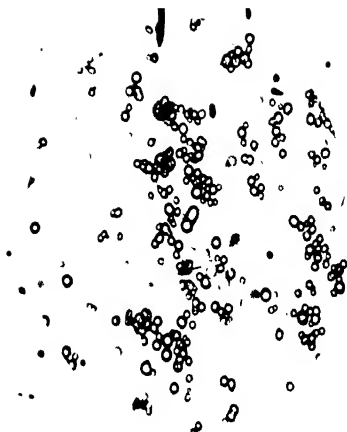


FIG. 18. TAPIOCA STARCH 110 DIA





DYERS' MATERIALS.

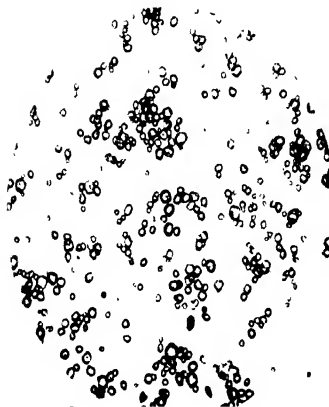


FIG. 19. MAIZE STARCH  $\times 110$  DIA.



FIG. 20. RICE STARCH  $\times 110$  DIA.







